# WORKSHOP ON THE PHYSICS AND CHEMISTRY OF MAGMA OCEANS FROM 1 BAR TO 4 MBAR

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# WORKSHOP ON THE PHYSICS AND CHEMISTRY OF MAGMA OCEANS FROM 1 BAR TO 4 MBAR

Edited by Carl B. Agee John Longhi

Held at Burlingame, California December 6-8, 1991

Sponsored by
Lunar and Planetary Institute
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3600 Bay Area Boulevard

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# **Preface**

Magma ocean: a unifying concept that ties together the earliest histories of the Moon, the terrestrial planets, and the asteroids, or a naive construction born of ignorance? Following the first Apollo mission the concept of a lunar magma ocean became firmly entrenched as a means of explaining the gross geochemical and petrological features of the Moon, although there was never any consensus as to its size, duration, or even its existence. Modeling of the dynamics of accretion led to the recognition that collisions between planet-sized objects were probable in the early solar system. Subsequently, a collision between a differentiated Mars-sized impactor and the proto-Earth has provided a popular explanation for the origin of the Moon that accounts for the similarity in oxygen isotopes in the Earth and Moon and for the apparent depletion of iron on the Moon. The aftermath of such a collision would have left much of the Earth molten and would have provided an environment in which the Moon could have accreted rapidly enough to form its own magma ocean. At the same time, recognition of very high formation temperatures in some iron meteorites, implying that their asteroid-sized parent bodies were molten, has suggested formation of magma oceans on smaller scales and by different mechanisms. These considerations, plus the recent advances in determining phase equilibria at very high pressures and in modeling the dynamics of strongly turbulent convection, provided a ready premise for a workshop on the physics and chemistry of magma oceans.

Evidence for the existence of magma oceans was discussed in great detail, and among the many new items introduced were high-pressure phase equilibrium experiments, calculations of depth of impact-produced melting, models incorporating crystal growth rates with degree of crystallinity and convection, and models of hard turbulent convection. If there was one point of agreement, it was that before we can point to some present-day observable parameters and confidently establish the existence of magma oceans, we must learn much more about their phase equilibria and solidification dynamics.

> Carl B. Agee, Harvard University John Longhi, Lamont-Doherty Geological Observatory



# Program

Friday, December	r 6, 1991				
8:45	Opening Remarks—C. Agee and J. Longhi, Conveners				
	SESSION I: EVIDENCE FOR AND AGAINST Chairman: P. H. Warren				
9:00	Keynote: Taylor G. J.* Norman M. D. Evidence for Magma Oceans on Asteroids, the Moon, and Earth				
9:45	Warren P. H.* Inheritance of Magma Ocean Differentiation During Lunar Origin by Giant Impact and Warren P. H.* Kallemeyn G. W. The Ferroan-Anorthositic Suite and the Extent of Primordial Lunar Melting				
10:10	Hillgren V. J.* Origin of the Moon and Lunar Core Formation				
10:45	Musselwhite D. S.* Drake M. J. Swindle T. D. Forsterite/Melt Partitioning of Argon and Iodine: Implications for Atmosphere Formation by Outgassing of an Early Martian Magma Ocean				
11:05	Murthy V. R.* Evidence for a High Temperature Differentiation in a Molten Earth: A Preliminary Appraisal				
SESSION II: PHASE EQUILIBRIA Chairmen: C. B. Agee and J. Longhi					
11:25	Keynote: Agee C. B.* High-Pressure Melting of Carbonaceous Chondrite				
12:30	Takahashi E.* Evidences for the Terrestrial Magma Ocean from High-Pressure Melting Experiments				
1:50	Herzberg C.* Phase Equilibria and Trace Element Partitioning in a Magma Ocean to 260 Kilobars				
2:10	McFarlane E. A.* Drake M. J. Gasparik T.  Mg-Perovskite/Silicate Melt Partition Coefficients in the CMS System at 2430°C and 226 kbars				
2:30	Drake M. J.* Rubie D. C. McFarlane E. A. Mg-Perovskite/Silicate Melt and Magnesiowüstite/Silicate Melt Partition Coefficients for KLB-1 at 250 kbars				
2:50	Ohtani E.* Yurimoto N. Terrestrial Magma Ocean and Core Segregation in the Earth				
3:30	Rubie D. C.* Ross C. R. II Carroll M. R. Elphick S. C. Estimation of the Viscosities of Silicate Liquids at High Pressure from Measurements of Oxygen Diffusivity				

<sup>\*</sup> Denotes speaker

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3:50 Jones J. H.\* Capobianco C. J. Drake M. J.

Estimation of High Temperature Metal-Silicate Partition Coefficients

4:10 Borisov A. Dingwell D. B.\* O'Neill H. St. C. Palme H.

Experimental Determination of the Solubility of Iridium in Silicate Melts: Preliminary Results

### POSTER PRESENTATIONS

#### Newsom H. E.

Pressure Regimes and Core Formation in the Accreting Earth

### PRESENTED BY TITLE ONLY

### Sasaki S.

Cooling of the Magma Ocean Due to Accretional Disruption of the Surface Insulating Layer

### Saturday, December 7, 1991

# SESSION III: DYNAMICS AND EVOLUTION Chairman: H. J. Melosh

9:00	Keynote: Stevenson D. J.*  Dynamics and Evolution of a Magma Ocean
9:45	Hansen U. Yuen D. A.* Zhao W. Malevsky A. V.  The Role of Hard Turbulent Thermal Convection in the Earth's Early Thermal Evolution
10:15	Solomatov V. S.* Stevenson D. J. Evolution of a Terrestrial Magma Ocean: Thermodynamics, Kinetics, Rheology, Convection, Differentiation
10:25	Abe Y.* Thermal Evolution and Chemical Differentation of the Terrestrial Magma Ocean
11:05	Morse S. A.* Fate of a Perched Crystal Layer in a Magma Ocean
11:25	Jolliff B. L.* A New Angle on Lunar Ferroan-Suite Differentiation
11:45	Snyder G. A.* Taylor L. A. Imperfect Fractional Crystallization of the Lunar Magma Ocean and Formation of the Lunar Mantle: A "Realistic" Chemical Approach
	SESSION IV: MECHANISMS OF FORMATION Chairman: T. J. Ahrens
1:45	Keynote: Kaula W. M.* Magma Ocean: Mechanisms of Formation
2:30	Tonks W. B.* Melosh H. J. Magma Ocean Formation Due to Giant Impacts
3:10	Wetherill G. W.* Giant and Large Impacts in the Context of Planetary Formation Theory
3:30	Jakes P.* Superheat in Magma Oceans

# Sunday, December 8, 1991

# SESSION V: GEOPHYSICAL CONSEQUENCES Chairman: B. R. Hawke

9:00	Keynote: Schubert G.* Early Planetary Differentiation: Geophysical Consequences
9:45	Ahrens T. J.* A Magma Ocean and the Earth's Internal Water Budget
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# **Summary of Technical Sessions**

# SESSION I: EVIDENCE FOR AND AGAINST

Summarized by P. H. Warren

The keynote paper for this session was by G. J. Taylor and M. D. Norman, with the talk given by Taylor. He reviewed the meteoritic evidence for widespread melting in many asteroids. Several different varieties of iron meteorites crystallized from molten, low-S masses of metal, thus implying attainment of temperatures high enough to engender highdegree melting of the silicate portions of the parent asteroids. The two groups of pallasite meteorites, which consist of metallic FeNi and FeO-poor olivine, but virtually no other silicates, are particularly likely to have formed in extensively molten asteroids (probably along core-mantle boundaries). The primary evidence for a lunar magma ocean is the observation that more than half the crust consists of highly anorthositic "ferroan" rocks, while complementary "ferroan" and mafic cumulates, which must have formed, are absent. These mafic complements apparently sank deep into the lunar interior beneath the buoyant anorthositic crust. The negative Eu anomalies of most mare basalts are plausibly modeled by assuming that their source regions were essentially these "missing" mafic cumulates, complementary to the ferroananorthositic component of the crust, which has a pronounced positive Eu anomaly.

Evidence for the earliest thermal state of the Earth is more equivocal. Theoretical arguments suggest that the Moon formed by a giant impact between the Earth and a Mars-sized body, in which case the Earth must have become totally molten. Suggestions have been made that elemental ratios in mantle samples can be used to confirm or deny the existence of a deep primordial magma ocean, but Taylor noted that the high-pressure petrologic data that constrain these models are still imprecise, and that for some elemental ratios the bulk composition of the Earth is poorly constrained. There is no single "chondritic" value for some key ratios, Taylor stressed. During discussion after this talk, P. H. Warren stated that despite Taylor's valid point about diversity among chondrites for some key ratios, for some combinations of elements (most notably the refractory lithophile elements) chondrites do have practically uniform ratios. Several people cautioned that evidence for widespread melting should not necessarily be taken as evidence for "magma oceans" on asteroids. Taylor agreed that semantically "magma ocean" might be an exaggeration for some of the asteroids he discussed, but he reiterated that at least for the case of the main-group pallasites, "magma ocean" seems appropriate.

The next talk, by Warren, addressed magma oceans on two bodies: the Moon and the putative Mars-sized impactor that was responsible for the origin of the Moon (and the total

melting of the Earth). Warren noted that in some models the derivation of matter to form the Moon is biased toward the outer fringe of the Mars-sized impactor. Consequently, differentiation within the impactor's magma ocean may have been inherited by the Moon. His models predict significant Moon/Earth fractionations for some ratios of refractory lithophile elements that are commonly assumed to be unfractionated (vs. chondrites) in both bodies. During discussion, C. B. Agee noted that the high-pressure crystal/melt distribution coefficients used by Warren have tremendous uncertainties. Warren agreed that the Moon/Earth fractionation factors are currently not well constrained, but he argued that significant fractionations seem inevitable, and that the high-pressure distribution coefficients should be improved soon.

The next talk was by V. J. Hillgren on mass balance for siderophile elements during lunar origin by O'Neill's 1991 version of the giant impact hypothesis, according to which the siderophile abundances in the Moon were established not only by combining impactor and proto-Earth material, but also by adding a late reduced veneer. Hillgren tested O'Neill's model by using thermodynamics to extrapolate from metal/basalt distribution coefficients measured at 1260°C to values appropriate for a lunar magma ocean temperature (~1670°C). These models assume that the lunar core formed at moderate oxygen fugacity, and is thus quite Ni-rich (35 wt% Ni). Models for Ni, Co, Mo, and W give good fits to the estimated lunar mantle abundances. Discussion afterward included some cautionary remarks concerning the uncertainties in the modeling.

The fourth talk of the morning was by D. S. Musselwhite, who presented a paper with M. J. Drake and T. D. Swindle on outgassing of noble gases from a primordial martian magma ocean. If the SNC meteorites are from Mars, Ar and Xe in the martian atmosphere are radiogenic relative to the martian mantle. With moderate extrapolation from their measured data, Musselwhite et al. infer that the melt I/Xe ratio probably increases during crystallization of a magma ocean. They hypothesize that after an early protoatmosphere on Mars was removed by impact erosion, the present atmosphere formed by outgassing of high-K/Ar, high-I/Xe magma ocean residuum. In contrast, the SNC meteorites are derived from relatively low-K/Ar, low-I/Xe cumulates produced during early stages of crystallization of the magma ocean.

The final talk of this session was by V. R. Murthy, who proposed that the terrestrial mantle siderophile element pattern was a byproduct of early magma ocean differentiation. Murthy noted the familiar paradox that when measured metal/silicate partition coefficients are applied to the Earth's mantle/core differentiation, the mantle is predicted to show

greater depletions of the most highly siderophile elements. such as Re and Ir, than are observed. He suggested that this problem might be resolved by using partition coefficients. extrapolated to high temperatures, which he derived by assuming proportionality to  $\exp(\mu_O/RT)$ , where  $\mu_O$  (inferred on the basis of the measured partition coefficients) is the chemical potential of the siderophile element in a hypothetical standard state at which the component at unit concentration has the properties that it would have at infinite dilution. Murthy's extrapolated high-T partition coefficients are shifted toward unity relative to the measured ones, and their application to the Earth predicts a mantle siderophile pattern that closely resembles the observed one. During discussion, J. H. Jones criticized Murthy's extrapolation method as oversimplified. Specifically, Jones asserted that Murthy's extrapolation implicitly shifts oxygen fugacity to higher values. Someone else noted that depletions of siderophile elements in the Earth's mantle were probably dampened, anyway, by late accretion accompanying the cratering of the lunar highlands, which remained intense until ~3.9 Ga.

### SESSION II: PHASE EQUILIBRIA

Summarized by C. B. Agee

Recent experimental results presented in this session emphasized the importance of high pressures and temperatures on the phase equilibria, element partitioning, density, and viscosity in a deep terrestrial magma ocean. The multianvil device is clearly the apparatus of choice for testing mantle melting scenarios. Seven of the nine papers presented in the session reported multianvil data relevant to magma ocean studies.

In the keynote talk C. B. Agee presented results from melting experiments on the Allende carbonaceous chondrite. Agee's experiments show that Fe<sup>+2</sup>-rich magnesiowüstite fractionation in an early magma ocean may have depleted the primordial mantle in Fe<sup>+2</sup> and contributed to the core formation process.

E. Takahashi reviewed some of his earlier work on peridotite melting at high pressures and compared this with melting temperatures of Allende carbonaceous chondrite. He proposed the peridotite liquidus as the upper bound for magma ocean temperatures and the Allende solidus as the lower bound. Takahashi noted the small dT/dP of peridotite and carbonaceous chondrite liquidi at high pressure and concluded that only a small increase in mantle temperature is needed to melt the Earth to considerable depths. He also made the interesting observation that if the existence of Archean komatiites is due to a potential mantle temperature (PMT) that was 300°C higher than today, then the existence of a deep terrestrial magma ocean in the Hadean is unavoidable.

C. T. Herzberg argued that to properly assess the importance of majorite garnet fractionation in formation of the peridotite upper mantle one must account for the effect of pressure on element partitioning. Herzberg pointed out that garnet fractionation at low pressure (10 to 16 GPa) yields liquids that are geochemically unlike peridotites, but at 20 to 26 GPa garnet is truly majoritic and may be subtracted from chondrite in a mass balance to produce peridotite.

E. A. McFarlane and M. J. Drake presented element partitioning data for mantle phases up to 25 GPa and 2400°C. They argued that Mg-perovskite fractionation is inconsistent with deriving present upper mantle refractory lithophile element ratios from chondritic values. Taken in isolation, their results do not favor an early magma ocean with large-scale perovskite fractionation. They noted, however, that when combined with magnesiowüstite fractionation, significantly larger amounts of perovskite fractionation may be allowable.

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E. Ohtani presented experimental data on partitioning of transition metal elements appropriate to early melting events and core mantle separation. He noted that the observed depletion of some transition metals in the mantle may be explained by a two-stage process. The first stage is the conventional silicate-metal equilibrium prior to separation and core formation. The second stage consists of downward segregation of dense ultrabasic liquid and magnesiowüstite into the core-mantle boundary.

D. C. Rubie reported preliminary results of the pressure effect on viscosity of silicate melts. The technique measures the diffusivity of tracer <sup>18</sup>O in silicate melt, which can be related to viscosity. Rubie showed that at 1800°C, viscosity of Na<sub>2</sub>Si<sub>4</sub>O<sub>4</sub> decreases in the interval 2.5 to 10 GPa by ~0.7 log units. Future work will apply this method to mantle melts.

J. H. Jones critiqued recent work by V. R. Murthy on the "excess siderophile element problem," and argued that Murthy's method of extrapolating low-temperature element partitioning data to very high temperatures was flawed. He concluded that it is not presently possible to achieve meaningful high-temperature estimates and that direct experimental measurements are required.

D. B. Dingwell gave preliminary results of attempts to measure the solubility of Ir in anorthite-diopside melts. This study, when complete, may contribute to understanding the behavior of chalcophile and/or siderophile elements during planetary core formation processes.

#### SESSION III: DYNAMICS AND EVOLUTION

Summarized by H. J. Melosh

The session on the dynamics and evolution of magma oceans was opened with a keynote address by D. J. Stevenson, who put the subject into the context of the fundamental physical processes affecting the behavior of a planetary-scale magma body as it cools from above the liquidus to complete solidification. While the physics of convection at the endpoints of either a completely molten magma ocean or a completely solidified mantle is now reasonably well understood, uncertainties are large at intermediate crystal contents. Stevenson and most other session participants agreed that little crystal-liquid separation can occur at high melt fractions because crystals are entrained in the vigorously convecting magma ocean, an idea pioneered by W. B. Tonks and H. J. Melosh in 1990. However, when the melt fraction decreases to the range 0.3-0.2, the crystals "lock up," the effective viscosity increases by many orders of magnitude, and the melt moves by percolation through the deformable crystal "mush." Chemical differentiation of the magma ocean may take place as the liquid percolates through the solid matrix, driven by density differences. Understanding of these processes is clouded by the current poor understanding of crystal growth rates, the rheology of partially molten solids, and the physics of crystal-liquid separation.

Y. Abe presented a one-dimensional model of magma ocean convection and differentiation, finding that compatible and incompatible element abundances may change during crystallization at melt fractions less than 0.3-0.2, but that the differentiation is not very sensitive to the precise values of the partition coefficients. He also noted that, because of the large viscosity variation at "lock up," a magma ocean spends most of its existence in the partially molten condition. V. S. Solomatov and Stevenson studied the evolution of a magma ocean from an initially liquid state to complete crystallization. They found that at low melt fractions Fe-rich liquids may settle to the core-mantle boundary while a primitive crust forms on top, but warned that Rayleigh-Taylor instabilities in the partially molten mush might rehomogenize the differentiated mantle. At melt fractions low enough for differentiation to occur, more crystalline phases are present than just the liquidus phase. They estimated that 107-109 years may elapse before complete solidification occurs, a time range indicative of the current uncertainty of the physics of magma oceans.

U. Hansen, D. Yuen, W. Zhao, and A. V. Malevsky discussed the role of the recently discovered "hard turbulence" convection regime appearing at Rayleigh numbers between 107 and 108. The relatively low viscosity (by subsolidus convection standards) partially crystallized "mush" is likely to have cooled in this regime. Hansen et al. showed that this type of convection is characterized by disconnected hot plumes rising toward the surface, and that it is much more sensitive to depth-dependent phase transitions than lower Rayleigh number convection, suggesting the possibility of layered convection in the hot, partially crystallized terrestrial magma ocean.

S. A. Morse analyzed the consequences of an internal septum of neutrally buoyant crystals, whose possible existence at a depth of about 250 km in the Earth has been suggested by recent theoretical and experimental studies of the relative density of melt and crystals at high pressure by Stolper, Walker, Rigden, Ahrens, Agee, and other workers. Morse found that such a septum is ephemeral, melting constantly at its base as olivine crystals sediment onto it from above, thus enriching the region below the septum in Fe and perhaps leading to an enrichment of refractory phases within the septum itself. The septum pumps heat from the lower to the upper convecting region and establishes the upper boundary condition for the underlying region.

Finally, two more traditional petrologic studies focused on the petrogenesis of lunar rocks. B. L. Jolliff argued that mafic ferroan rocks from the lunar highlands may have been derived from liquids trapped in floating plagioclase cumulates, rather than, as previously supposed, from a deep magma ocean. G. A. Snyder and L. A. Taylor modeled trace-element evolution in a crystallizing lunar magma ocean. Their model incorporates trapping of about 1% of residual liquid in the sinking mafic cumulate and entrainment of 2-5% plagioclase in the convecting magma, the remainder of which floats to form the highland crust. They obtain late-stage liquids similar to K-rich KREEP, and conclude that convective overturn of the final layered mantle is not required to explain the chemistry of the lunar highland rock suite.

# SESSION IV: MECHANISMS OF FORMATION

### Summarized by M. J. Drake

W. M. Kaula opened the session with a keynote talk in which he outlined the terrestrial environment during the final phase of the accretion of the Earth and pointed out some interesting consequences of differing catastrophic events for the Earth and Venus. Metal accreting to the Earth would have quickly sunk to the core, and a giant impact may have ejected silicates beyond the Roche limit where they accreted to form the Moon. These final accretionary events were sufficiently energetic to raise the temperature of the Earth by several thousand degrees, enough to vaporize silicates. A strong planetary wind may have carried off volatiles and some silicate material hydrodynamically. If Venus did not experience a moon-forming giant impact, perhaps it did not develop such an intense wind, accounting for its much higher volatile content relative to Earth (e.g., Ar is 80 times more abundant). A magma ocean would inevitably have been formed on the Earth. Vigorous turbulent convection in the crystallizing magma perhaps limited the efficiency of degassing such that subsequent release of water from the solidified mantle might account for the present water oceans. The difference in primordial noble gas concentrations between Earth and Venus suggests only limited addition of volatiles from the outer solar system could have occurred after the moon-forming impact into the Earth.

After this sweeping introduction, W. B. Tonks and H. J. Melosh discussed the formation of magma oceans during giant impacts. The critical variables to be considered are the impact velocity, the radius of the impactor, and the gravity of the target. The amount of melt generated increases with increases in the value of each variable. The fraction of melt retained below the excavation zone is important because excavated melt would rapidly cool and would be unlikely to contribute to the formation of a magma ocean. Tonks and Melosh calculate that the impact of a Mars-sized body into the Earth would create a magma ocean of approximately 300 km if the velocity of the impactor corresponded to the escape velocity of the Earth. This depth increased to about 2000 km if the velocity of the impactor was about 20 km/s. The ability to form magma oceans is strongly dependent on target mass. Magma oceans of 30-100 km could be generated by impact on the Moon of a projectile of one-tenth lunar mass, while impacts into asteroid-sized targets are incapable of forming deep magma oceans.

G. W. Wetherill reviewed the current state of planetary formation theory. The early stages of growth were probably characterized by rapid growth (10<sup>5</sup> years) of planetary embryos of Moon to Mercury size, leading to a trimodal distribution of matter, Moon-to-Mercury-sized embryos, partly grown planetesimals of radius 5–50 km, and collisional fragments extending in size down to micrometer scale. The embryos reached sufficient mass to gravitationally perturb one another such that their orbits crossed and their relative velocities increased. Over 10<sup>8</sup> years these embryos collided, swept up smaller material, and assembled themselves to form the present planets. These later stages of accretion involved many impacts by objects a significant fraction of the mass of the target. Magma ocean formation is a plausible outcome of these events.

Finally P. Jakes discussed the implications of superheated magma oceans. The most important effects are on transport phenomena, which will become more vigorous, and on volatile loss, including oxygen, which will result in both loss of traditional volatile elements and reduction of FeO-bearing phases resulting in the production of metal. These volatility-related phenomena are observed in natural superheated objects such as tectites, impact glasses, and fulgurites.

A view is emerging in which the Earth was substantially molten during and subsequent to acquiring most of its present mass. Volatiles were lost from a hot silicate vapor-bearing atmosphere through hydrodynamic or some other form of escape. The magma ocean convected turbulently and vigorously, inhibiting both segregation of crystallizing silicate and oxide phases and volatile transport. The former had the effect of leaving no chemical trace of the crystallization pro-

cess, while the latter may have served as the reservoir from which the present water oceans and other volatiles were derived.

### SESSION V: GEOPHYSICAL CONSEQUENCES

Summarized by B. R. Hawke

In this session three talks were presented that dealt with both the geophysical and tectonic consequences of magma oceans on the terrestrial planets. G. Schubert presented a comprehensive keynote talk concerning the geophysical consequences of early planetary differentiation. He noted that the differentiation of a planet can have profound consequences for its structure and thermal evolution, and stated that recent theories for the origin and evolution of the Moon and the terrestrial planets indicate that these objects formed hot and subsequently cooled, and that early core formation and, in the cases of the Earth and Moon, a very deep magma ocean are characteristic features of these models.

S. C. Solomon and other workers have argued against the cooling of Mars and the Moon from hot initial states with very deep magma oceans on the basis of expected tectonic consequences of thermal contraction. Schubert indicated that the old view for Mars was that extension and global expansion dominated martian thermal history. This view implies a cold initial state and late core formation. He stated that it is now believed that extensional tectonic features are largely associated with the regional deformation of Tharsis. In addition, the new view emphasizes that wrinkle ridges, which are prominent in martian ancient terrain, reflect the global compressional deformation associated with secular cooling and contraction.

In the case of the Moon, it has been argued that the lack of compressional tectonism comparable to Mercury's thrust faults in scale and distribution limited the thermal contraction of the Moon to less than about 1 km since the end of heavy bombardment at about 3.8 Ga. The thermal contraction of an initially molten Moon strongly violates this constraint. However, a magma ocean with a depth of 200-300 km and an initial lunar central temperature of ~500°C leads to a thermal history consistent with this constraint. In contrast, A. Binder and co-workers have argued that the existence of young (<1 Ga), 10-km-scale highland thrust faults and shallow moonquakes are indicators of significant contraction of the Moon and of cooling from an initially molten state. It was noted in the discussion session of this talk that many lunar geologists question the scale of the thrust faults described by Binder and co-workers. While most agree that these features represent thrust faults, it is questionable that they exhibit the suggested degree of offset.

It was noted that Kirk and Stevenson have taken a new look at the stress history of the Moon. They have presented results of a new aproach in calculating lunar volume change during cooling. These workers concluded that the observed paucity of tectonic features is consistent with the Moon being ~50% molten.

Finally, Schubert noted that the lunar center of masscenter of figure offset could reflect either the asymmetric distribution of the crust or the asymmetric distribution of density anomalies in the mantle. The crustal asymmetry may have been produced by thermal convection, which swept crustal material preferentially into one hemisphere.

P. H. Warren presented a very interesting talk concerning the three stages of magma ocean cooling. The first stage of magma ocean (MO) cooling is an era of radiative heat loss from the surface. The cooling rate during this stage is limited by the degree of convection within the magma ocean. Warren pointed out that if the MO is insulated by a dense atmosphere, or if the heat source of the MO is continually replenished, the length of this first stage of cooling is difficult to predict. Otherwise, calculations indicate that a chill crust will form within a few decades of the time of maximum melting.

This initial stage lasts until a chill crust forms. During this second stage, heat loss is limited by conduction through the crust. Warren noted that during this stage, the MO is still cooling and that the thickness of the mantle cumulate zone is increasing at a rate up to several orders of magnitude faster than the rate of crustal thickening.

The third stage of cooling begins when the near-surface MO composition evolves to the point of saturation with feldspar. Warren stated that a thick, flotation crust cannot form until a phase buoyant at low pressure begins to crystallize and that the only candidate is feldspar. The MO cannot crystallize appreciable feldspar until the melt composition is sufficiently enriched in alumina to be feldspar saturated. The MO cooling rate precipitously declines in stage three and the rate of crustal thickness growth as a function of temperature suddenly increases. Finally, Warren summarized the various implications of his three-stage model of magma ocean cooling and crystallization.

The final talk of this session presented the results of remote sensing studies of the distribution and modes of occurrence of lunar anorthosite. B. R. Hawke noted that if the Moon once had a magma ocean, an anorthositic crust should have been produced by plagioclase flotation and that a critical question is where there is an enrichment in plagioclase in the lunar crust. Hawke summarized the spectral evidence for the occurrence of pure anorthosite on certain rings of Orientale, Humorum, Grimaldi, and Nectaris Basins as well as the central peaks of Alphonsus and Petavius Craters. The distribution of anorthosite on the lunar nearside exhibits a very interesting pattern. Anorthosites have only been identified in a relatively narrow zone extending from Petavius in the east to the Inner Rook Mountains on the western limb of the Moon. Hawke noted that extensive spectral studies of many nearside regions have failed to reveal additional deposits of pure anorthosite.

Hawke emphasized that lunar anorthosite deposits are almost always found on or very near impact basin rings and that an important objective of this study was to obtain an understanding of the significance of this correlation. He concluded that this association is important only for the inner rings of basins such as Orientale and Grimaldi. The Inner Rook ring and the inner ring of Grimaldi appear to be composed, at least in part, of pure anorthosite that was derived from beneath a more mafic-rich layer in the preimpact target sites. At Orientale and Grimaldi, the inner-ring massifs are composed of anorthosite exposed by small, fresh impact craters on the rings or simply on the steep slopes of the massifs. In contrast, the anorthosites associated with the outer rings of Nectaris and other basins are found in the central peaks and walls of large impact craters. These anorthosites appear to have been derived from layers many kilometers beneath the crater target sites.

Hawke concluded that in those areas that exhibit anorthosites, the anorthosites were exposed from beneath a shallower layer of more pyroxene-rich material. Although this upper unit is more mafic than the anorthosite layer, it still contains abundant feldspar. A major challenge for future studies is to develop and test models for the formation of this stratigraphic sequence.

# **Abstracts**

# N92-28588

THERMAL EVOLUTION AND CHEMICAL DIFFERENTIATION OF THE TERRESTRIAL MAGMA OCEAN; Y. ABE, Water Research Institute, Nagoya University, Nagoya, 464-01 JAPAN.

Release of gravitational energy results in global melting and formation of a magma ocean during accretion of the Earth<sup>(1,2)</sup>. Although it is believed that formation of the magma ocean resulted in gravitational differentiation of melt and solid, the differentiation might be disturbed by the following processes: (1) Convective mixing. (2) Cooling and solidification. (If solidification proceeds very rapidly, the magma ocean might be "quenched" in an undifferentiated state). (3) Growth of the Earth, which results in (a) secular increase of pressure, and (b) stirring by planetesimal impacts. The purpose of this study is to investigate the differentiation processes of the terrestrial magma ocean by taking into account various disturbing processes shown above.

We assume spherical symmetry and local thermal equilibrium between melt and solid phases. We take into account melt-solid differentiation, convective heat-mass transportation, melt-solid phase change, and viscosity variation with melt fraction. Chemical differentiation is monitored by calculating transportation of compatible and incompatible trace elements. Convective transport is calculated by using the mixing length theory<sup>(3)</sup>. Melting relations are estimated<sup>(1)</sup> based on Ohtani<sup>(4)</sup>.

We consider the evolution of magma ocean formed by a giant impact at first. We choose an adiabatic temperature gradient as the initial temperature profile and ignore growth of the Earth. (Differentiation process is less affected by the impact stirring<sup>(5)</sup>). Figure 1 shows evolution of the vertical profiles of temperature and melt fraction at 1 million year interval. Since we assumed no atmosphere, very rapid cooling occurred in the upper part of the magma ocean and the melt fraction decreased to less than 0.3 within 1Ma. Then cooling slowed down and melt fraction was kept at  $0.2 \sim 0.3$  for more than 4Ma at shallower part. This slow down of cooling rate was caused by increase of viscosity in partial melt. Although differentiation is disturbed by convective mixing at high melt fraction<sup>(6)</sup>, it proceeds efficiently at this melt fraction<sup>(7)</sup>. Figure 2 shows the time evolution of trace element distribution. Melt-solid partitioning of elements are expressed by using partition coefficients defined by

$$K_i \equiv \frac{(concentration \ of \ element \ i \ in \ solid \ phase)}{(concentration \ of \ element \ i \ in \ melt \ phase)}$$

We assume that partition coefficients are constant and initial distribution of elements is uniform. We consider three incompatible elements  $(K_i < 1)$  and two compatible elements  $(K_i > 1)$ . Although element distribution pattern is completely different between compatible element group and incompatible element group, it is quite similar within each group in spite of large difference in  $K_i$  value. Thus, the element distribution does not directly reflect difference in partition coefficients. Quite similar results are obtained, even if we start the calculation at low melt fraction  $(\phi = 0.1)^{(7)}$ .

The following conclusions are obtained<sup>(7)</sup>:

(1) Because of large viscosity variation in partial melt, the magma ocean is tend to be kept at intermediate melt fraction.

(2) When magma ocean is vigorously convecting, chemical differentiation proceeds most

efficiently at intermediate melt fraction.

(3) Hence, chemical differentiation seems to be inevitable, if density difference exists between solid and melt, and the partition coefficients are not unity.

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- (4) Chemical differentiation is controlled by composition difference between melt and solid at intermediate melt fraction, rather than that at liquidus or solidus.
- (5) The resulted elemental distribution does not always reflect difference of partition coefficients. Moreover, it is insensitive to  $K_i$  values in some cases.
- (6) Thermal and chemical evolution is rather insensitive to the initial condition.

We assumed that the solid phase is always denser than the melt in this study. However, preliminary calculation, which is not shown here, suggests a possibility of homogenization caused by the density cross over in the magma ocean. Further investigation is required on this problem.

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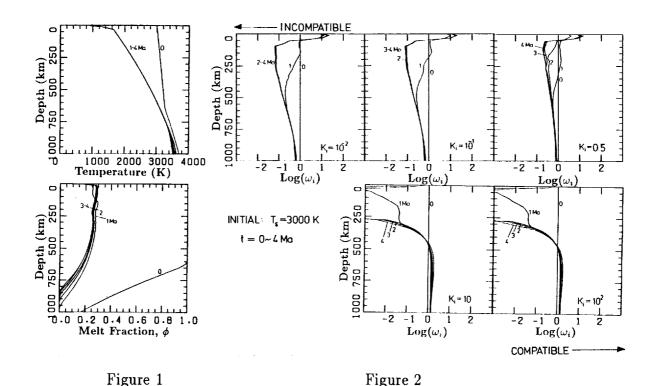


Figure 1: Time evolution of the temperature and melt fraction distribution<sup>(7)</sup>.

Figure 2: Time evolution of trace element concentration profiles<sup>(7)</sup>.

# HIGH-PRESSURE MELTING OF CARBONACEOUS CHONDRITE

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Phase equilibria experiments investigating the melting and differentiation of the primordial Earth require a realistic "initial" chemical composition. Carbonaceous chondrites are good analogues for the initial bulk chemical composition of an accreting early Earth because they contain approximately solar abundances of the non-volatile elements and are the most primitive objects yet sampled in the solar system. In contrast, modern peridotites may be derivative and therefore not compositionally relevant to the earliest stage of Earth formation.

One of the the ways in which carbonaceous chondrites differ chemically from modern upper mantle peridotites, is that they are much more FeO-rich1. FeO-rich in this case implies iron in the ferrous state, for the most part, as an essential structural component in silicate minerals. (In fact, very little of the iron in carbonaceous chondrite resides in the metallic state [e.g. ~1 wt% in Allende CV3], the only other major Fe-bearing phase aside from silicates is an Fe,Nisulfide similar in composition to pendlandite which can make up some 7 wt% of the bulk meteorite). If subjected to crustal or shallow mantle conditions the stable ferro-silicates in a carbonaceous chondrite are primarily olivines and pyroxenes. At higher pressures in the deeper mantle it is expected that ferrous iron resides in garnet, silicate spinel, silicate perovskite, and magnesiowüstite. It has been a commonly held belief that this "excess" ferrous iron in a chondritic Earth was removed from the silicate mantle and segregated as metallic iron to form the core2. Such a mechanism however, could not have operated at the oxygen fugacities present in today's upper mantle and certainly could not have operated in a body similar to carbonaceous chondrite, the most oxidized of the primitive chondrites. A requirement for Fe (Ni, Co, and other moderately siderophile elements) extraction from silicate minerals to form a core the size of present Earth's is to invoke a highly reducing oxidation state during the early mantle-core evolution3. Had the present mantle undergone a single stage reduction reaction to form the core in this way, then a geochemical signature might be evident in the samples of upper mantle peridotites. These hypothetical peridotites would contain olivines with forsterite contents of 98 mol% versus the 90 mol% actually observed, and both Ni+2 and Co+2 would be wholly missing from the mantle4, rather than being at ~1000's (Ni) and 100's (Co) ppm trace levels often recorded in xenoliths. To remedy the unrealistically low oxidation state produced in these models, an adhoc late-stage bombardment of fresh oxidized meteoritical debris is commonly included in the scenario<sup>3,4</sup>. This oxidized component is meant to penetrate and mix with the mantle in order to boost the oxygen fugacity back up to appropriate levels.

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As an alternative to the "two component" oxidation state model for mantle differentiation and core formation, multi-anvil experiments which I have performed recently at 24, 26 and 26.5 GPa<sup>5</sup> on the Allende meteorite suggest that it may be possible to segregate iron from the primordial mantle to form the core without invoking a highly reduced oxidation state. Instead, a large portion of the iron reaches core depths and is incorporated there not as Fe(Ni)-metal but as Fe(Ni)-sulfide and Fe-oxide. The ultrahigh-pressure multi-anvil experiments show that FeO-rich magnesiowüstite is an abundant crystallizing phase at temperatures near the silicate liquidus in carbonaceous chondrite. Coexisting with this silicate-oxide phase assemblage is a microprobe determined Fe<sub>0.41</sub> Ni<sub>0.10</sub> Re<sub>0.01</sub> S<sub>0.48</sub> liquid phase. If a chondritic Earth experienced a high-temperature molten stage, then during cooling and crystallization, the segregation of the densest phases (molten Fe, Ni-sulfide and FeO-rich crystalline magnesiowüstite) to the deepest levels of the interior could occur. It is proposed that magnesiowüstite fractionation may have depleted the initial FeO content of the primitive chondritic mantle and contributed to the formation of the Earth's core.

This first approach to the experimental problem assumes for simplicity that the Earth accreted from 100% carbonaceous chondrite. Because carbonaceous chondrites are the most oxidized of the chondrites, this model also results in the maximum oxygen in the core. If for instance, the model is modified to include some ordinary and enstatite chondrites to the mix, then the amount of oxygen in the core may be lower. The variability of sulfide, carbon and hydrogen contents in chondrites may also be addressed in a similar way to explain the "light" element budget for the core.

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A MAGMA OCEAN AND THE EARTH'S INTERNAL WATER BUDGET;
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There are at least three lines of evidence which relate bounds on the primordial water content of the Earth's mantle to a magma ocean and the accompanying Earth accretion process. We assume initially (before a magma ocean could form) that as the Earth accreted, it grew from volatile- (H2O, CO2, NH3, CH4, SO2, plus noble) gas-rich planetesimals, which accreted to form an initial "primitive accretion core" (PAC) (Fig. 1). The PAC retained the initial complement of planetesimal gaseous components. Shock wave experiments in which both solid [1], and more recently, the gaseous components of materials such as serpentine and Murchison meteorite [2 and unpublished data] have demonstrated that at planetesimal infall velocities of < 0.5 km/sec, induce shock pressures of < 5 GPa and result in virtually complete retention of planetary gases (Fig. 2). A 0.5 km/sec infall velocity corresponds to an escape velocity of a ~800 km radius for the Earth's initial PAC. Using the water content of Orguel to estimate the water-content of planetesimals, the PAC is modeled as containing a maximum of ~1.5 oceans of water and other volatiles such as <sup>3</sup>He which were subsequently mixed with degassed material, but still retain the primordial signature in today's mantle (e.g. Davies [3]). The fraction of the Earth which accreted under Mode A (iron silicate forming conditions) can be estimated to be 12 to 22% based on the observed Fe/(Fe + Mg) content of the present mantle. Further accretion caused partial devolatilization of H2O and other volatiles from planetesimals into the primitive atmosphere leaving behind ~6.5 oceans in a partially devolatilized PAC, (PDPAC). Thus, as the Earth grew in radius from ~800 to ~2,000 km, chemical conditions changed from Mode A accretion [4] (oxidized surface materials and reduced atmosphere) in which the oxygen fugacity is approximated by the wüstite-magnetite, fayalitemagnetite-quartz or magnetite-hematite buffer [5] to Mode B. As modelled by Abe and Matsui [6, 7] and later by Zahnle et al. [8], their work indicates that a hot massive water and CO<sub>2</sub> atmosphere covered the Earth. This accretion is Mode B. Commencing at a primordial Earth radius of ~2000 km, a magma ocean formed and planetesimals which impacted the Earth at 2-3 km/sec were sufficiently shock heated to deliver all the planetesimal volatile budget into this atmosphere. ~1,500K magma ocean for which 78 to 88% of the Earth accreted under Mode B conditions is buffered by the solidus of water-rich basalt. The high temperatures are achieved via impact heating near the surface and the heat is retained by the "blanketing" infrared radiatively opaque atmosphere. Moreover, the mass of the metallic iron components which impacted onto the magma ocean are augmented by the rapid reaction of iron silicate to iron metal. Recently, experiments conducted by Rowan and Ahrens [9] demonstrate rapid reaction of Fe+2 to Fe and diffusion from molten silicate into the metal phase at low oxygen fugacity. The increase in oxygen fugacity of the atmosphere in going from ~300 to 1500 K for a C1 carbonaceous chondrite composition assumed here, and also by Abe [5], is in accord with thermochemical calculations of Holloway [10]. The depths to which the magma ocean could have formed on the Earth is really unknown and appears to be constrained in models of accretion by the infall rate of planetesimals, their size distribution, and water content. Initial primitive water content arising from the high solubility of water within molten basalt modelled by Fricker and Reynolds [11] is supported by later work of Kadik et al. [12] and indicates that from 0.1 to 1% water is soluble in molten basalts with H<sub>2</sub>O pressures of ~1 to 10<sup>2</sup> MPa. Thus, three constraints on the primordial water budget of the Earth are a legacy of the magma ocean: (1) the ~1.5 oceans in the PAC and 6.5 oceans in the PDPAC inferred from shock wave experiments., (2) The present day <sup>3</sup>He flux of 3 atom/cm<sup>2</sup>/sec is consistent with a PAC undepleted reservoir made-up of a water-rich primitive meteorite-like material with a water content similar to Orguel and a chondritic <sup>3</sup>He/H<sub>2</sub>O ratio. Such a primitive accretion core based on the <sup>3</sup>He flux provides 1.5 oceans of water with the assumption that the presently observed flux was continuous from 4.65 Æ to the present time. (3) The dissolved surface water in the magma ocean is expected to be stabilized at great depth by the vigorous convection envisioned by, e.g. Tonks and Melosh [13]. Moreover, the magma appears to have an increasing potential solubility for water with pressure. Upon eventual cooling of a magma ocean water could be taken up in either anhydrous mantle minerals [14] and a growing family of hydrous high-pressure phase minerals

[15, 16, 17]. The freezing of a magma ocean prior to a loss of its primitive atmosphere could provide as much as 30 ocean masses of primordial water in the mantle.

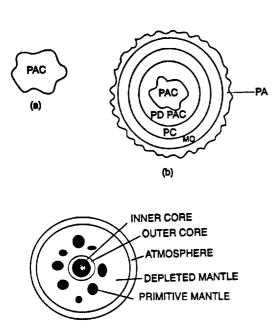


Fig. 1. Diagrammatic sketch of the three phases of Earth accretion. a) Formation of a primitive accretion core (PAC). This is an ~800 km radius proto-Earth for which the infall velocity is so low (≤0.5 km/s) that virtually no impact volatilization occurred. Subsequent accretion does incur partial volatile loss from infalling planetesimals. b) A very idealized proto-Earth when it has substantially accreted but before substantial core segregation and core infall has taken place. The PAC is surrounded by a partially devolatilized primitive accretion core (PDPAC), that in turn is surrounded by a partially segregated primitive liquid core (PC) which in turn is surrounded by a magma ocean which is covered with a massive proto-atmosphere. c) The Earth today. Fragments of primitive mantle, derived from the PAC are shown, distributed in the mantle but preferentially located in the less vigorously convecting lower mantle.

(c)

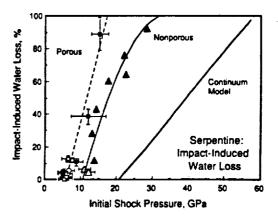


Fig. 2. Impact-induced water loss as a function of initial shock pressure for nonporous and porous (20%) porosity) serpentine [2]. Filled squares, solid recovery method, porous serpentine; open squares, gas recovery method, porous serpentine; open circles, gas recovery method, deuterium-enriched serpentine; filled triangles, solid recovery method, nonporous serpentine; open triangles, gas recovery method, nonporous serpentine. Solid lines labelled Porous and Nonporous, empirical fits to data for porous and non porous serpentine. Solid line labelled Continuum Model. Devolatilization for nonporous serpentine calculated using the shock entropy model, assuming ambient water vapor pressure conditions of 50% humidity at 25°C.

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EXPERIMENTAL DETERMINATION OF THE SOLUBILITY OF IRIDIUM IN SILICATE MELTS: PRELIMINARY RESULTS. Alexander Borisov<sup>1</sup>, Donald B. Dingwell<sup>2</sup>, Hugh St.C. O'Neill<sup>2</sup> and Herbert Palme<sup>3</sup>. Academy of Sciences of the USSR, Vernadsky Institute of Geochemistry, Laboratory of Mantle Geochemistry, Kosygin St. 19, SU-117975, Moscow, Russia; Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, W8580 Bayreuth, Germany; Max Planck Institut für Chemie, Abteilung Kosmochemie, Saarstraße 23, Postfach 3060, W6500 Mainz, Germany.

#### INTRODUCTION:

Little is known of the geochemical behavior of Iridium. Normally this element is taken to be chalcophile and/or siderophile so that during planetary differentiation processes, e.g. core formation, Iridium is extracted from silicate phases into metallic phases. Experimental determination of the metal/silicate partition coefficient of Iridium is difficult simply because it is so large (e.g. Rammensee, 1978). Also there are no data on the solubility behavior of Iridium in silicate melts. Is Iridium dissolved as metal, as IrO2 or as some other species in silicate melts? With information on the solubility of Iridium in silicate melts it is possible, in combination with experimental data for Fe-Ir alloys, to calculate the partition coefficient between a metallic phase and a silicate melt.

#### METHOD:

We have determined the solubility of Iridium in melts in the system diopside — anorthite using two different methods. In the first method the sample of melt is held by surface tension in a cylinder of Iridium metal and allowed to equilibrate in a CO-CO2 gas mixing tube furnace at high temperatures. In the second method the liquid sample is held in an Iridium crucible and stirred with an Iridium spindle to promote equilibrium, also in a gas mixing tube furnace, (using CO-CO2 and O2-Ar). The first type of experiment is performed as time series at each temperature and fO2 and the samples are sectioned to test for diffusion-controlled concentration gradients. Equilibrium can be demonstrated using these techniques. In the second method a single large batch (70 g) of liquid may be cycled up and down temperature and fO2 in an individual experimental run. The melt is sampled as a time series at individual steps of temperature and fO2 and reversals may be achieved. Iridium contents are determined by neutron activation analysis.

### **RESULTS:**

Preliminary results have been obtained using both methods in air for various compositions in the system anorthite-diopside and in the temperature range of 1350 to 1600°C. Iridium concentrations under all investigated conditions are relatively constant (4 to 25 ppm). Given the free energy of formation of IrO2(c), these results indicate that the low solubility of Iridium is due in part to very high activity coefficients for IrO2 in silicate melts.

Using the first method we have obtained a result indicating 70 ppb of Iridium in a diopside-anorthite melt at  $1350^{\circ}$ C and log10 fO2 = -7.14 (0.35 log10 units below QFM). Extrapolating our results obtained in air to this low fO2, assuming that Iridium remains dissolved in the melt as IrO2 (i.e.,

tetravalent), predicts Iridium solubilities in the parts per trillion range; extrapolation assuming IrO (i.e., divalent) predicts solubilities from 3 to 15 ppb, in reasonable agreement with our preliminary results.

In any case, the present results are not compatible with those of Amossé et al. (1990) who have reported a strong decrease in Iridium solubility with increasing fO2. Those experiments were, however, conducted on Fe-bearing silicate melts. The development of submicroscopic Fe-Ir alloys could explain the discrepancy between those results and the present data.

#### DISCUSSION:

The solubility of Iridium in silicate melts appears to be sufficiently high that the precipitation of Os-Ir (±Ni ±Fe) nuggets from mantle-derived mafic and ultramafic melts probably does not occur in nature, but our calculation is close enough, considering the unknown effects of FeO and other compositional variables on Iridium solubility, coupled with the likely range of fO2 of natural melts, that the possibility cannot be completely dismissed.

The extrapolation of Ir solubilities to lower fO2s must be uncertain until the valence state(s) of Iridium in silicate melts is established. However, assuming divalent Ir and a constant activity coefficient and taking the activity coefficient of Ir in Fe metal to be 0.01 (Hultgren et al., 1973) we predict  $D_{\rm Ir}^{\rm met/sil} \cong 10^{12}$  at 1350°C, log10 = -10.6. This value is several orders of magnitude greater than the lower limits for  $D_{\rm et/sil}^{\rm met/sil}$ 

measured by Rammensee (1978). The high relative concentration of Ir in the earth's mantle (0.8±0.4% CI) is therefore about 9 orders of magnitude too high to have been in equilibrium with the iron-rich metal of the earth's core (at least at these temperatures and pressures). This discrepancy would also seem to be much too large to be eliminated by higher temperatures or pressures (i.e. metal segregation under lower mantle conditions), therefore supporting the notion originally put forward from the chondritic relative abundances of the highly siderophile elements for the addition of a late veneer to the earth's mantle after the last episode of core formation (e.g. Chou, 1978).

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Mg-PEROVSKITE/SILICATE MELT AND MAGNESIOWÜSTITE/SILICATE MELT PARTITION COEFFICIENTS FOR KLB-1 AT 250 KBARS. Michael J. Drake\*, David C. Rubie#, and Elisabeth A. McFarlane\*. \*Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721, U.S.A; #Bayeriches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, 8580 Bayreuth, GERMANY.

### **INTRODUCTION:**

The partitioning of elements amongst lower mantle phases and silicate melts is of interest in unraveling the early thermal history of the Earth. Because of the technical difficulty in carrying out such measurements, only one direct set of measurements has been reported previously (Kato et al., 1988), and these results as well as interpretations based on them have generated controversy (Walker and Agee, 1989). Here we report what are to our knowledge only the second set of directly measured trace element partition coefficients for a natural system (KLB-1). A companion abstract reports on parallel experiments in the synthetic CMS system (McFarlane et al., 1991a).

# **EXPERIMENTAL:**

An experiment using KLB-1 (kindly donated by E. Takahashi) doped with V, Cr and Mn was run at ~2400°C and ~250 kbar using a 1200 ton multianvil apparatus at the Bayerisches Geoinstitut. A 7 mm MgO (+5 wt. % Cr<sub>2</sub>O<sub>3</sub>) octahedron was used together with 3 mm truncation edge lengths on the WC anvils. The sample was contained in a Re capsule which also acted as the heater and which was contained within a LaCrO<sub>3</sub> sleeve for thermal insulation. Temperatures close to the center of the sample were measured up to ~2000°C with a W3%Re/W25%Re thermocouple placed in contact with the heater wall, and the final temperature reached was estimated from an extrapolation of the power-temperature relationship. The pressure estimate is based on calibrations performed at 1800°C. Due to the eventual failure of the Re heater the run duration was only 30 seconds and, because the sample became locally contaminated with La (~6 wt. %) and Cr (~5 wt. %) from the LaCrO<sub>3</sub> sleeve, partition coefficients for La and Cr cannot be considered reliable. The resulting run product contains a sequence of phase assemblages from below the solidus to above the liquidus along the thermal gradient in the sample. Because the liquidus was not situated at the center of the sample, the liquidus temperature is at present uncertain but must be less than 2400°C.

# ANALYTICAL:

The charge was mounted in epoxy and analyzed using CAMECA SX-50 electron microprobes in Bayreuth and Tucson. Standard operating conditions were employed, although counting time for the less abundant elements was increased to improve counting statistics. The melt is unquenchable, and forms a dendritic intergrowth of quench crystals and residual melt. It was analyzed using a 30µm raster. The structural identity of the Mg-perovskite phase was confirmed using X-ray microdiffractometry at Universität Bayreuth. Magnesiowüstite is also present, but the possible existence of other phases in the subliquidus region has not yet been studied.

#### **RESULTS:**

Mg-perovskite/silicate melt and magnesiowüstite/silicate melt partition coefficients are given in the Table 1, along with the results of other workers. Partition coefficients for Mg, Al, and Si deviate more from unity than those of McFarlane et al. (1991a) and of Kato et al. (1988) obtained at slightly different temperatures, pressures, and/or compositions, while the converse is true for Ca (see Table 1 of McFarlane et al., 1991a). Partition coefficients for V suggest that it is slightly incompatible in Mg-perovskite. This result is in loose agreement with the results of Ohtani. et al. (1991) who use an indirect method to conclude that V is somewhat more incompatible. Our results for Mn and Fe also indicate that they are incompatible in Mg-perovskite, although less so than calculated by Ohtani et al. (1991).

# Mg-Perovskite/Melt and Magnesiowüstite/Melt Partitioning

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Magnesiowüstite/silicate melt partition coefficients for Mg, Al, and Si agree well with those of McFarlane et al. (1991b). Vanadium and Mn appear to be compatible in magnesiowüstite, in contrast to the somewhat incompatible behavior calculated by Ohtani et al. (1991). There is general agreement that Fe and Cr are compatible in magnesiowüstite.

These results must be treated with caution because Walker and Agee (1989) have pointed out that the strong temperature gradient in charges such as reported here can lead to thermal (Soret) diffusion in the silicate melt, raising questions concerning whether even a close approach to equilibrium was achieved. The discussion of this problem in McFarlane et al. (1991a) also applies here.

## **DISCUSSION:**

The partition coefficients reported here for a natural KLB-1 composition indicate that segregation of Mg-perovskite from melt during a magma ocean stage early in Earth history will lead to significant fractionation of ratios of refractory lithophile elements. See Figure 1 of McFarlane et al. (1991a) for an illustrative calculation.

The abundances of V, Cr, and Mn in the mantles of the Earth and Moon are very similar to each other, and decrease in the order V>Cr>Mn (Drake et al., 1989). This similarity may have implications for the origin of the Moon (Ringwood et al., 1990, 1991). Attempts to explain these abundances through metal/silicate fractionation at pressures from 1 bar to 165 kbars have failed, as have explanations appealing to differential volatility, although Ringwood et al. (1990, 1991) propose that these abundances were established by metal/silicate equilibrium at megabar pressures. This suggestion remains to be tested. The results in Table 1 suggest that Mg-perovskite fractionation is unlikely to play a role in the establishment of these abundances, but magnesiowüstite fractionation might account in part for their depletion.

TABLE 1. Mg-Perovskite/Melt and Magnesiowüstite/Melt Partition Coefficients

Mg-Perovskite/melt		Magnesiowüstite/melt			
	This Work	Ohtani,'91	This Work	Ohtani, '91	McFarlane, 1991b
	250 kbar	270 kbar	250 kbar	230 kbar	160 kbar
	<2400°C	1700°C	<2400°C	2400°C	2225°C
	measured	calculated	measured	calculated	measured
Mg	0.8	*	2.1	*	2.0
Al	2.3	*	0.2	*	0.3
Si	1.9	*	0.01	*	0.01
Ca	0.7	*	0.03	*	*
V	0.9	0.2	1.6	0.9	*
Cr	*	0.4	*	1.4	2,2
Mn	0.8	0.05	1.9	0.5	*
Fe	0.4	0.1	3.1	1.6	1.5
	* not measure	d			

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# The Role of Hard Turbulent Thermal Convection in the Earth's Early Thermal Evolution

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In the last several years there has been great progress made on the study of a new transition in thermal convection, called hard turbulence. Initial experiments were conducted with helium gas, then with water. It was shown that for base-heated Newtonian convection a transition occurred at Rayleigh numbers between 107 and 108. This transition is characterized by the appearance of disconnected plume structures in contrast to continuous plumes with mushroom-shaped tops found for lower Rayleigh numbers, 0(106). This new hydrodynamic transition is expected to play an important role in reshaping our concepts of mantle convection in the early stages of planetary evolution. We have conducted twodimensional calculations for large and small aspect-ratio configurations to see whether such a transition would take place for infinite Prandtl number fluids. Our numerical simulations, carried out to Ra=1010, show that for Newtonian convection and Ra exceeding 107 mushroom-like plumes become disconnected ascending instabilities. These high Ra flows consist of large scale cells with strong intermittent boundary-layer instabilities. nonlinear rheology the transition to the disconnected plume regime occurs at lower Nusselt numbers than for Newtonian convection. In this disconnected-plume regime, layered convection is more likely, as the effects of phase-boundary distortion are lessened by the homogenization of the thermal anomalies in the interior. The olivine to spinel phase-transition, which is destabilizing from linear theory, induces layered convection, as Ra is increased beyond 107. Layered convection is more likely to have taken place in the young Earth, when Ra was much greater than today.

THE DISTRIBUTION OF ANORTHOSITE ON THE NEARSIDE OF THE MOON; B.R. Hawke, P.G. Lucey, and G.J. Taylor, Planetary Geosciences, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI 96822. P.D. Spudis, Lunar and Planetary Institute, Houston, TX 77058.

### INTRODUCTION

If the Moon once had a magma ocean, an anorthositic crust should have been produced by plagioclase floatation. A critical question is whether there is an enrichment in plagioclase in the lunar crust. Hence, it is important to determine the distribution and modes of occurrence of anorthosite on the lunar surface.

In recent years, we have been conducting remote sensing studies of lunar basin and crater deposits in order to determine the composition of surface units and to investigate the stratigraphy of the lunar crust. 1,2,3,4 We have combined both visible and near-IR spectral observations with multispectral imaging in order to determine the lithology of relatively small portions (2-10 km) of the lunar surface. Numerous deposits of pure anorthosite (plagioclase >90%) have been identified and an interesting pattern has emerged. The purposes of this report are 1) to summarize the results of our previous studies of the distribution of anorthosite, 2) to present new findings concerning the modes of occurrence of lunar anorthosite, and 3) to assess the implications for the magma ocean hypothesis.

### DISTRIBUTION AND MODES OF OCCURRENCE

Orientale Basin Region: With the exception of the Inner Rook massifs, all the highlands units inside the Orientale basin appear to be composed of either noritic anorthosite or anorthositic norite.  $^{1,2}$  The Inner Rook Mts. are markedly different. Our previous data indicated that two of these mountains are composed of pure anorthosite. Multispectral imaging data confirm this view; the entire eastern Inner Rook Mts. contain only minute amounts of low-Ca pyroxene. Thus, it appears that the Inner Rook ring of the Orientale basin is a mountain range composed of anorthosite. The plagioclase absorption band (~1.25  $\mu m$ ) occurs in some spectra, but not in all, suggesting either different shock histories or different plagioclase compositions for various portions of the Inner Rook ring.

Humorum Basin Region: Humorum is a large multiringed impact structure on the southwestern portion of the lunar nearside. The most complete ring of the basin is 440 km in diameter and bounds Mare Humorum.<sup>5</sup> At least a portion of this mare-bounding ring of Humorum is composed of pure anorthosite. Spectra were collected for Mersenius C (diameter = 14km) and the Gassendi E and K complex. These small impact craters expose fresh material from beneath the surface of massifs in the mare-bounding ring. The "1µm" absorption features in these spectra are extremely shallow. Only very minor amounts of low-Ca pyroxene are present in the areas for which these spectra were obtained; an anorthosite lithology is indicated. Anorthosite also appears to have been exposed by Liebig A, a 12-km impact crater on the western portion of the mare-bounding ring. However, this entire ring is not composed of anorthosite, and to date no anorthosites have been identified on the outer Humorum ring.

Grimaldi Basin Region: Grimaldi is a small (430 km) two-ringed impact basin. We have obtained one spectrum of an anorthosite from a portion of the inner ring. Other spectra for the inner ring exhibit a very shallow pyroxene absorption feature, which indicates the presence of very minor amounts of orthopyroxene. These areas may also prove to be composed of anorthosite.<sup>2</sup> Another anorthosite deposit has been identified just inside the outer Grimaldi ring. Apparently, this anorthosite was excavated from beneath the Grimaldi floor material by subsequent impacts. Other highlands deposits emplaced in the Grimaldi region as a result of the Orientale impact event appear to be composed of noritic anorthosite.<sup>2</sup>

Nectaris Basin Region: While noritic anorthosites and anorthositic norites are the

dominant rock types in the region, anorthosite deposits have been identified.<sup>3</sup>, <sup>4</sup> Bohnenberger F is a small (10km) impact crater on an elongated highland massif inside the Montes Pyrenaeus ring of the Nectaris basin. Neither of the two spectra obtained for Bohnenberger F exhibits the well-defined "1µm" absorption feature seen in spectra for typical fresh highland craters that expose pyroxene-bearing rock types.<sup>3</sup>, <sup>4</sup> Bohnenberger F exposed a deposit of nearly pure anorthosite. Anorthosite also occurs in two areas on the east wall of Kant crater (33 km) which is located on a platform massif of the main Nectaris basin ring.<sup>3</sup> We have also found anorthosite deposits in two areas within Cyrillus A crater (17 km). Moreover, Pieters<sup>6</sup> found additional anorthosite deposits in the central peaks of Piccolomini and Theophilus craters. Anorthosites have now been identified on, or very near, the four innermost rings of Nectaris.

Other Occurrences: Anorthosites have also been identified in the central peaks of Alphonsus and Petavius craters.<sup>6,7</sup> Both of these craters are very near major rings of ancient impact basins.<sup>8</sup>

#### DISCUSSION

The distribution of anorthosite on the lunar nearside exhibits a very interesting pattern. To date, anorthosites have only been identified in a relatively narrow zone extending from Petavius in the east to the Inner Rook Mts. on the western limb. Extensive spectral studies of many nearside regions (e.g., Imbrium, northern central highlands) have failed to reveal additional deposits of pure anorthosite.1,2,3,6,7 However, few spectra have been obtained for some nearside regions (e.g., east limb, northern highlands, southern and southeastern portions of the central highlands), and analyses of the Apollo orbital geochemistry data sets suggest that anorthosites may be located in selected areas (e.g., Smythii basin).

The results of this study indicate that lunar anorthosite deposits are almost always found on or very near basin rings. An important objective of this effort has been to obtain an understanding of the significance of this correlation. We have concluded that this association is important only for the inner rings of basins such as Grimaldi and Orientale. The Inner Rook ring and the inner ring of Grimaldi appear to be composed, at least in part, of pure anorthosite that was derived from beneath a more mafic-rich layer in the pre-impact target sites. It is important to note that at Orientale and Grimaldi, the inner ring massifs are composed of anorthosite. These anorthosites are exposed by small, fresh impact craters on the rings or simply on the steep, relatively young slopes of the massifs. In contrast, the anorthosites associated with the outer rings of Nectaris and other basins are commonly found in the central peaks and walls of large impact craters. These anorthosites were derived from layers many kilometers beneath the crater target sites. It does not appear that surfaces of these outer rings are composed of anorthosite although such material must exist at depth.

Finally, the results of our spectral studies have important implications for the stratigraphy of the lunar crust in those areas that exhibit anorthosites. In every instance, the anorthosites were exposed from beneath a shallower near-surface layer of more pyroxene-rich material. This is usually noritic anorthosite (plagioclase 80-90%) or, less commonly, anorthositic norite (plagioclase 70-80%). While this unit is more mafic than the anorthosite layer (commonly >90% plagioclase), it still contains abundant feldspar. The thickness of this more pyroxene-rich layer ranges from a few kilometers to tens of kilometers. A major challenge for future studies is to develop and test hypotheses for the formation of this stratigraphic sequence.

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PHASE EQUILIBRIA AND TRACE ELEMENT PARTITIONING IN A MAGMA OCEAN TO 260 KILOBARS; Claude Herzberg, Department of Geological Sciences, Rutgers University, New Brunswick, NJ 08903 (908 932-3154)

A magma ocean can solidify in a way that is intermediate between perfect equilibrium and perfect fractional crystallization. In order to model quantitatively any fractional crystallization scenario, it is necessary to understand the geochemical characteristics of the phases that crystallize from a magma ocean, and how they vary with pressure. The crystallizing phase is called the liquidus phase, and their identities have been determined by numerous experiments utilizing the multianvil apparatus (1,2,3,4,5,6). For chondritic compositions the liquidus phases are: olivine at 1 atmosphere to 100 kilobars; garnet from 100 to about 260 kilobars; silicate perovskite from 260 kilobars to possibly the core-mantle boundary in the Earth.

Garnet and silicate perovskite phases are pyroxene-like in chemistry. Fractionation of either of these phases (low MgO/SiO<sub>2</sub>) from a magma ocean with chondritic geochemistry (intermediate MgO/SiO<sub>2</sub>) provides a means of deriving mantle peridotite as a residual liquid (high MgO/SiO<sub>2</sub>). Variations on this theme were advanced by Ohtani and Sawamoto (1,2), Ito and Takahashi (4), Agee and Walker (5,8,9), and Herzberg & coworkers (7,10,11). But garnet and perovskite fractionation models must also explain the full spectrum of geochemical observations, all major and trace elements. Kato, Ringwood, and Irifune (12,13) attempted to show that neither garnet nor silicate perovskite fractionation could have occurred because they would have fractionated the lithophile major and trace elements to concentrations that are not observed in mantle peridotite. If correct, their conclusion that garnet and perovskite fractionation did not occur can be viewed as evidence against the hypothesis that a terrestrial magma ocean formed by accretion of planetesimals, especially by giant impacts.

There has been considerable debate about this problem. Agee and Walker (8,9) noted that the perovskite-liquid partition coefficients reported by Kato et al. (12) did not support perovskite fractionation, whereas the set of coefficients reported later by Kato et al. (13) did support it; Agee and Walker also appealed to olivine addition to tighten the mass balance. There was agreement, however, that garnet fractionation was not important (8,12), a conclusion based largely on liquidus garnets synthesized at about 160 kilobars.

Additional experimental data have been acquired during the past 2 years, and they are helping to clarify the debate on garnet and perovksite fractionation. Part of the confusion emerged from an insufficient understanding of the effect of pressure on the geochemistry of garnet at high pressures. Liquidus garnets are: "pyropic" (Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>; 22-24 % Al<sub>2</sub>O<sub>3</sub> and 3 % CaO) in the low pressure range (100 kilobars); pyroxene-like or "majorite" (MgSiO<sub>3</sub>; 4 to 8 % Al<sub>2</sub>O<sub>3</sub>) in the highest pressure range (200-260 kilobars); pyrope-majorite (eg., 16 % Al<sub>2</sub>O<sub>3</sub>) at intermediate pressures. Pressure has a strong effect on the partitioning between garnet and liquid of all major as well as trace elements. In a recent paper by Herzberg and Gasparik (7), an experimental calibration was reported for the partitioning of CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> between garnet and liquid. It was demonstrated that primitive mantle peridotite could not have formed as liquid by garnet fractionation in the 100 to 160 kilobar range; however, it could have formed as a liquid by about 35 % majorite fractionation from a CV chondrite like Allende in the 200 to 260 kilobar range. Removal of moderate amounts of majorite to the lower mantle during the crystallization of a magma ocean is a successful way of explaining differences in MgO/SiO<sub>2</sub> and CaO/Al<sub>2</sub>O<sub>3</sub> between mantle peridotite and chondrite.

The large pressure-induced changes in the geochemistry of liquidus garnet is now becoming apparent in other ways. Unpublished data show that FeO and MgO partitioning changes substantially,  $K_D$  changing from 0.9 at 25 kilobars to about 0.3 at pressures in excess of 150 kilobars  $[K_D = (Fe/Mg)_{CR} \times (Mg/Fe)_{L}]$ . There also appear to be large changes in the partition coefficients for

the rare earth elements between gamet and liquid. Partition coefficients calculated for gamet/liquid at 250 kilobars from the perovskite/liquid & perovskite/gamet data of Kato et al. (12,13) are much lower than those observed at 160 kilobars, and look very pyroxene-like (D's for the HREE < 1). Partition coefficients for gamet at 160 kilobars are also very different from pyrope at 30 kilobars. Although we are not yet secure with a reliable set of  $D_{MjA}$  for lithophile trace elements at 200 to 260 kilobars, the data of Kato et al. (12,13) indicate that 35 % majorite fractionation in this high pressure range will not substantially fractionate the lithophile trace elements; Sc/Sm = 0.77; Sm/Yb = 1.15 are predicted. Of an extensive data base that I have examined, only the very primitive peridotite SC1 described by Jagoutz et al. (14) comes closest to having these characteristics (Sc/Sm = 0.79; Sm/Yb = 1.27).

Any unambiguous geochemical test of majorite and perovskite fractionation must be based on truly primordial samples of mantle peridotite. By definition, this could be material that solidified from a magma ocean that lost 35 % majorite, material that was then isolated from subsequent remelting events over the last 4.5 billion years of Earth history. Peridotite sample SC1 comes closest to this definition. However, when modified by a small amount of partial melting with pyrope in the residue, the geochemical identity of primordial mantle is readily destroyed. Forward modeling yields Sc/Sm = 1 and Sm/Yb = 1 for 5 % partial melting, an unusual peridotite residue because it has the illusion of being pristine like chondrite or pyrolite. A possible example of this material is peridotite Ib8 reported by Stosch & Seck (15; Sc/Sm = 0.98; Sm/Yb = 1.06). For degrees of partial melting in excess of 5 %, peridotite residues adopt the characteristics of the present-day MORB source region (Sc/Sm > 1; Sm/Yb < 1). These results, together with the naturally-occurring peridotite SC1, question the commonly-held assumption that primordial mantle is identified by lithophile trace elements in chondritic proportions.

In summary, garnet fractionation from chondrite at relatively low pressures (100 to 160 kilobars) involves pyrope-majorite, and yields a residual liquid composition that does not match the major or trace element geochemistry of mantle peridotite. However, garnet fractionation at 200 to 260 kilobars is truly majoritic in terms of its pyroxene-like geochemistry, and is a very successful way of forming mantle peridotite from chondrite. These results are fully consistent with the idea that a magma ocean developed during the birth of the Earth, and that majorite fractionation occurred during that time.

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ORIGIN OF THE MOON AND LUNAR CORE FORMATION; Valerie J. Hillgren, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721

Introduction. Newsom (1,2) has shown that the abundances of siderophile elements in the lunar mantle may be accounted for by the formation of a small core at low degrees of partial melting of the silicate mantle. This result is inconsistent with the existence of a lunar magma ocean and with the conclusion that high degrees of silicate partial melting are necessary for the segregation of small amounts of metal (3,4). However, several assumptions made in this earlier work may have contributed to this paradox. For example, it was assumed that the lunar core is composed entirely of Fe and that metal segregation occurred at very low oxygen fugacities (i.e., 2 log units below the IW buffer). Recent work, however, suggests that the lunar core may be Nirich and may have formed at higher oxygen fugacities (5,6). In addition, initial abundances of siderophile elements in the lunar mantle in these models were assumed to be either chondritic or identical to the abundances in the Earth's mantle. However, the giant impact theory implies that the initial abundances of the siderophile elements in the lunar mantle can be a combination of the siderophile element abundances in the terrestrial mantle and in the mantle of the impactor implying that they do not need to be either strictly chondritic or identical to the terrestrial values. In a recent version of the giant impact hypothesis by O'Neill (6) the initial abundances of the siderophile elements in the lunar mantle were established not only by combining impactor material and proto-Earth material, but also by adding a late reduced veneer. O'Neill also appealed to the possible volatilities of some elements (i.e., Mo and W) under conditions of lunar accretion, and required the segregation of a small Ni-rich metallic core.

Hillgren (7) utilized Ni, Co, Mo and W partition coefficients obtained at 1260°C for systems containing Ni-rich metal to examine O'Neill's proposal. The results indicated that a 1 wt.% lunar core would contain between 35 and 45 wt.% Ni, and that Mo and W must be initially depleted relative to Ni and Co (presumably due to volatility as proposed by O'Neill(6)). In addition, approximately 75% partial melting of the silicate mantle was required consistent with the

existence of a lunar magma ocean.

There will not be 75% partial melting of peridotites at 1260°C, the temperature at which the partition coefficients were measured. Here I attempt to model more rigorously lunar core formation in the O'Neill scenario by correlating degree of partial melting to temperature and extrapolating the 1260°C partition coefficients to the appropriate temperatures along a constant redox buffer.

Partition Coefficients. The partitioning of Ni, Co, Mo, and W between Ni-rich metal and basaltic liquids at 1260°C at 1 bar pressure as function of oxygen fugacity has been experimentally determined (7). For modeling purposes, it is necessary to extrapolate the partition coefficients to the temperatures of interest. This was done by writing a simple exchange reaction:

$$MO_{y} \leftrightarrow M + \frac{y}{2}O_{2}$$
 (1)

and then applying the standard definition of the free energy of formation to derive the following expression:

$$\frac{-\Delta G^{\circ}}{2.303RT} = -\text{Log}(\gamma_{\text{M}}/\gamma_{\text{MO}_{\circ}}) - \text{Log}D_{\text{MET/SIL}} - \frac{y}{2}\text{Log}fO_{2} + \text{Log}f$$
 (2)

where R is the gas constant; T is the temperature in K;  $\gamma$  is the activity coefficient;  $D_{MET/SIL}$  is the metal/silicate partition coefficient, and f is a factor for conversion from molar to weight ratios  $(f\sim1)$ . If D and  $\Delta G^{\circ}$  for a given temperature and  $fO_2$  are known, then the ratio of the activity coefficients can be calculated. This activity coefficient ratio can then be used to calculate D at another temperature if a  $\Delta G^{\circ}$  at that T is known. Free energies of formation were taken from Robie et al. (8), and in some cases had to be extrapolated over a short temperature range. This method was tested by taking the data of Schmitt et al. (9) at 1300°C and predicting partition coefficients at

1600°C. Predictions agreed with measurements to within a factor of 2 to 3. Results of 25

extrapolations at constant redox buffer can be found in Table 1.

Solid silicate/liquid silicate partition coefficients for Ni and Co were interpolated from the olivine/melt data compiled in Irving (10) at the appropriate temperatures. Because Mo and W are both highly incompatible elements, values of 0.01 were adopted for the solid silicate/liquid silicate partition coefficients at all temperatures. These values are also given in Table 1.

Results and Discussion. Simple mass balance following the method of (7) was used to calculate an abundance pattern of Ni, Co, Mo, and W in the lunar mantle based on the assumed initial abundances of O'Neill (6) and the separation of a 1 wt.% metallic core that consists of 35 to

45% wt.% Ni. All input parameters for one particular model are shown in Table 1.

Degree of partial melting of silicates and temperature were correlated using a formulation by McKenzie and Bickle (11) for melting of peridotites at any pressure. I have chosen 1 bar for the pressure simply because the partition coefficients used in the model were measured at 1 bar. The pairs of temperature and degree of partial melting used in the calculations are shown in Table 1.

Degree of partial melting of the metal was assumed to be 0.5 for temperatures below the melting point of metal, and 1.0 for temperatures above. However, other calculations showed the degree of melting of the metal had essentially no effect on the results. Also varying the solid silicate/liquid silicate D between upper and lower limits consistent with the data presented in (10) had little effect on the results.

Results for the case of 35 wt.% Ni in the metal are shown in Figure 1. Results for 45 wt.% Ni in the metal are similar. In both cases good fits are obtained for the abundances of Ni, Co, Mo, and W in the lunar mantle at 75% partial melting of the silicates. The high degree of partial melting required for the O'Neill model to be viable is consistent with segregating small amounts of metal and a lunar magma ocean.

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Figure 1:

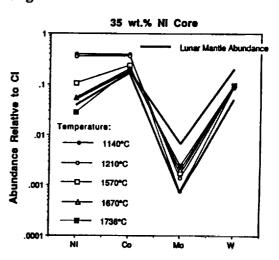


TABLE 1. Input parameters for calculation where core contained 35 wt.% Ni ( $fO_2=0.9$  units below IW). Initial abundances relative to CI are: Ni = 0.43, Co = 0.44, Mo = 0.073, W = 0.097. T is temperature; P is degree of partial melting of silicates; SM is solid metal; LM is liquid metal; LS is liquid silicate, and SS is solid silicate.

			D(NI)		1	D(Co)			D(Mo)			D(W)	_
<u>T</u>	Р	SM/LS	LM/LS	SS/LS									
	•												
1140	0.11	3600	2900	368	370	250	28	1300	930	0.01	2.7	0.26	0.01
1210	0.25	3200	2600	172	330	230	17	1600	1100	0.01	3.0	0.3	0.01
1570	0.51	2100	1700	10	220	150	2.5	3100	2200	0.01	5.2	0.5	0.01
1670	0.75	1900	1540	5.6	200	140	1.7	3700	2600	0.01	6.0	0.6	0.01
1736		1800	1470	4.0	190	130	1.4	4100	2800	0.01	6.6	0.65	0.01

SUPERHEAT IN MAGMA OCEANS. Petr Jakes, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058 and Department of Geosciences, University of Houston, Houston TX 77204.

Planetary formation through accretion processes in short times  $(10^6 - 10^8 \text{ years})$  supplemented by the separation of metal phases and core formation, results in their partial or complete melting (1). Even small bodies were probably melt differentiated (2,3), i.e., metal-sulphide melt was separated from silicate melt or silicate crystal residuum.

Collisions of planetesimals and particularly of large bodies (Mars-sized objects) with the forming planet (e.g., Earth), as implied by the accretionary hypothesis (4) result in the relatively high heat contents of planetary bodies and hence the formation of magma oceans. The heat is stored and if the thick atmosphere forms the heat dissipation is slow. Although the early evidence for the magma oceans came from petrological and geochemical observations (5,6) of lunar rocks, the concept has been extended to the other (inner) planetary bodies, though the extensive melting in the Earth has been often disputed.

The existence of "totally molten" planets implies the existence of a superheat (excess of heat) in the magma reservoirs since the heat buffer (i.e., presence of crystals having high latent heat of fusion) does not exist in a large, completely molten reservoir. Any addition of impacting material results in increase of the temperature of the melt and under favorable circumstances heat is stored. The behavior of superheat melts is little understood, however. We have therefore examined experimentally properties and behavior of excess heat melts at atmospheric pressures and inert gas atmosphere.

Highly siliceous melts  $(70\% \, \mathrm{SiO}_2)$  were chosen for the experiments because of the possibility of quenching such melts into glasses, the slow rate of reactions in highly siliceous composition, and the fact that such melts are present in terrestrial impact craters and impact-generated glasses. Experimental melting at superheat conditions and atmospheric pressures of inert gas  $(N_2 \, \mathrm{Ar})$  (7.8) shows:

- (a) The change of the structure of the melts with increasing temperature appears in the Raman spectroscopy analysis. This change is sudden and step-like, and we believe that the changes result from temperature-induced depolymerization of melts or change of the major component's coordination; it may result from the reduction of Si (volatilization of oxygen).
- (b) The changes of transport properties. Although we have found that the change of viscosity with increasing temperature is non-Arrhenian (nonlinear), we have not been able to demonstrate that the changes of viscosity correlate with "structural" (Raman spectroscopy indicated) changes.
- (c) The volatilization of alkali elements and oxygen content, which are indicated by the change of Na and K content in glasses from long-duration (or extremely high-temperature) experiments and by the presence of Fe-metal phase (and probably the presence of Si metal).

Similar changes were observed in natural objects that were subjected in the past to excess heat: tektites, impact melts, fulgurites, and ablation meteoritic spherules. These observations and results of experimental studies are applied to accretion heating and totally molten planets.

The natural consequence of the accretionary process is the occurrence of relatively large "impacting bodies" in the later stages of accretion, i.e., in a stage of a magma ocean. The accretionary theory and observations on "asteroid bodies" suggest that two types of impactors could be expected: (1) preheated and already differentiated planetesimals and (2) primitive and probably small (carbon-bearing and thus reducing) (9) bodies. Both types of bodies will increase the heat content of the target, causing both volatilization and reduction, though the reducing capabilities of carbon-bearing projectiles are much higher and will result in the presence of metallic phases and formation of CO or CO<sup>2</sup> atmospheres.

It is likely that large planetesimal bodies are "preheated" and that in a preheated planet with a magma ocean the kinetic energy of the impacts substantially increases the temperature of the target (magma ocean). The latent heat of fusion of the principal components of the ultramafic silicate rock (olivine) corresponds roughly to the increase of 400° of already molten material. The heat contribution of even small bodies can locally bring the temperature of a magma ocean well above the liquidus to a superheat state.

The changes of transport properties due to superheat in a localized region will cause vigorous motion within the magma reservoir and probably fast cooling of the upper boundary layer, though some volatilization of alkali elements Na and K (at liquidus  $+200^{\circ}$ C) and volatilization of iron and silica may take place (liquidus  $+500^{\circ}$  and  $+700^{\circ}$ C, resp.) (10) and may form a thick insulating atmosphere. Therefore the cooling effect may be delayed.

The temperature-induced reduction represents an another phenomenon that results from structural

changes (change of coordination number) within the superheat melts: The process may be also viewed as oxygen volatilization. Reduction of iron-oxide-bearing phases (accompanied by the reduction of moderately siderophile elements such as V, Cr, Mn, and Mo) and, at even higher temperatures, the reduction of silica (in the absence of Fe) could be expected. Similar high-temperature reduction is observed in the natural objects: in the tektite and impact glasses (11), fulgurites (12), and ablation micrometeoritic spherules (13) or experimental high-temperature heating, silicate materials (14) or in some highly reduced meteorites, (e.g., enstatite chondrites (with high contents of Si) or unequilibrated chondrites (15).

High-temperature volatilization and superheat-induced reduction have a coupling effect. The silicate and metal melt became immiscible but the reduced metal cannot sink since the convective motion of fluid is faster then the velocity of sinking of the denser phase; on the other hand, the near-surface volatilization at low pressures is more effective at turbulent conditions. Only after the Roses number (which compares the velocity of sinking of denser phase versus the convective motion of the medium) is less than 1 does the immiscible reduced metal phase sink, thus contributing to the core formation because of the small density difference between the silicate melts and silicate crystals, the differentiation of such a magma ocean is delayed into the late stages of cooling.

Both volatilization and reduction contribute to the compositional change in superheat magma reservoir (magma ocean) by depleting the reservoirs in the volatile fraction (K, Na, Fe, Si) and also in the siderophile elements (Fe, Cr, V, Mn, Ni, Si?) and enriching the reservoir in the refractory elements (e.g., Ca, Al, Th, U, Zr). The geochemical features corresponding to the high-temperature volatile and siderophile depletion are observed in the "bulk moon" composition (volatile and siderophile element poor), though only slightly demonstrated in the composition of the upper mantle of the Earth. Accepting the hypothesis that the Moon formed as a result of collision of the proto-Earth and the large (Mars-sized) object, one can speculate that such an event has taken place at an early stage of Earth formation: at 70 - 80% of the Earth accreted from hot strongly differentiated volatile-poor and reduced Earth mantle. In such a scenario the upper and lower mantle of the Earth represent two independent poorly communicating reservoirs. The lower mantle, which has been totally molten in early stages, is strongly reduced refractory-rich, volatile- and siderophile-element-depleted, whereas the upper mantle represents less reduced, only partially molten "chondritic" material added at the chilled lower mantle reservoir after the formation of the Moon.

Superheat in the magma ocean of early planets thus contributes to core formation, may account for compositional and redox heterogeneities of the mantle reservoir, and also contributes to the formation of the early atmospheres. The early atmospheres may have been wiped off by the "large cataclysmic events" (e.g., collision with the Mars-sized body), the event which substantially increased the temperature of the Earth and contributed (due to the loss of the atmosphere) to the chill effect zone, creating thus the base for the lower to upper mantle thermal and chemical discontinuity.

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A New Angle on Lunar Ferroan-Sulte Differentiation. B. L. Jolliff, Dept. of Earth & Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130

Small fragments of rock found among soil particles in sample 67513 from Station 11 on the southern rim of North Ray Crater at Apollo 16 yield information regarding the mafic, ferroan rocks from which they derive. We have identified a set of particles that have distinctive trace element geochemistry and whose bulk and mineral compositions indicate a genetic relationship to one another. These include polymict as well as monomict lithologies. Igneous members range from fragments with abundant anorthite to some with abundant exsolved pigeonite and augite. Consideration of this set of rock fragments, combined with mafic ferroan clasts from large breccias and from lunar-highlands meteorites suggests that there may be separate differentiation trends within the ferroan suite [cf. 1,2] which are subparallel and which are less steep in Fe-Mg vs. An fractionation than the vertical trend obtained when the entire ferroan suite is taken together. This may result from a complex magma system with isolated reservoirs or separate, independently evolving magmas. Mineral compositional and textural variations are consistent with a model set forth by Longhi and Boudreau [3] wherein the anorthite-rich samples reflect adcumulus growth with mafic crystals forming only from trapped liquid, and the more mafic samples by anorthite and pyroxene orthocumulate development.

<u>Data.</u> A set of fragments composing ~1/3 of a split of 2-4 mm soil particles from sample 67513 have high Sc/Sm ratios, i.e., >17 (Fig. 1), characteristic of ferroan-suite materials [4]. They also have high values of FeO/CaO and Sm/Yb and have been interpreted as a ferroan, mafic component of Descartes material [5]. Petrographic investigations of a subset of the soil particles show similarities to clasts in breccia 67076 [6] and 67215 [7], and it is likely that the soil particles are fragments of or derive from a common precursor.

The particles include coarse-grained (0.5-2 mm crystals) igneous fragments ranging in mode from over 90% anorthite (3 ppm Sc) to nearly 70% pyroxene (42 ppm Sc); however, no special significance is attached to the modes of individual particles. The most pyroxene-rich sample contains several percent ilmenite and probably a substantial trapped liquid component. Pyroxenes are exsolved and in several samples bulk pyroxene compositions prior to exsolution can be determined. In one sample, there is evidence for early cumulus pyroxene growth at about 1250°C (geothermometer of [8]) followed by adcumulus growth 50 to 80° lower (Fig. 2). Plagioclase crystals are coarse and retain minor compositional zoning (e.g., 2 An units). Olivine is present in minor amounts in the more anorthite-rich fragments; moderate CaO concentrations (0.1-0.3 wt.%) suggest shallow plutonic origins. The igneous fragments are pervasively fractured, but retain cumulus textures.

Interpretations. Could the igneous particles be small fragments of an anorthositic boulder or an otherwise very localized feature? Complex, polymict breccia particles in 67513 contain clasts of igneous-textured minerals whose compositions and assemblages relate them to the igneous particles. This observation and the fact that similar clasts have been found in large Apollo 16 breccias mean that the igneous precursor(s) had a history that included impact and breccia formation prior to excavation of North Ray Crater. Some of the particles from 67513 have compositions that to a first approximation can be interpreted as mixtures of materials rich in incompatible trace elements (ITE) and a material with the mean composition of the high Sc/Sm set of particles. This suggests that the latter component was widespread in its original location and that when it was mixed with other materials, it was as material with an average composition of about 5-8 ppm Sc.

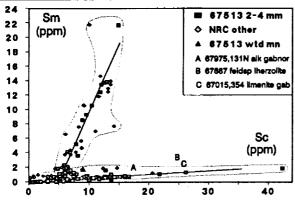


Figure 1. Plot of Sm and Sc concentrations (ppm) in 67513 particles. "NRC other" from [11,12,13,14].

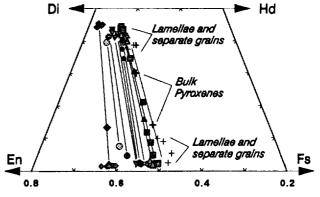


Figure 2. Pyroxene compositions in high Sc/Sm samples. Tie-lines join Px in each sample.

ESTIMATION OF HIGH TEMPERATURE METAL-SILICATE PARTITION 30 COEFFICIENTS. John H. Jones, SN2, NASA/JSC, Houston, TX 77058; Christopher J. Capobianco, and Michael J. Drake, Lunar and Planetary Lab., U. of Arizona, Tucson, AZ 85721.

It has been known for some time (e.g., Ringwood, 1966) that abundances of siderophile elements in the upper mantle of the Earth are far in excess of those expected from equilibrium between metal and silicate at low pressures and temperatures. Murthy (1991a) has reexamined this "excess siderophile element problem" by estimating liquid metal/liquid silicate partition coefficients at high temperatures. The metal/silicate partition coefficients estimated by Murthy are markedly reduced from their measured values at lower temperature, implying that siderophile elements become much less siderophilic at high temperature. Murthy then draws the important conclusion that metal/silicate equilibrium at high temperatures can account for the abundances of siderophile elements in the Earth's mantle. Of course, his conclusion is critically dependent on the small values of the partition coefficients he calculates. Because the numerical values of most experimentally-determined partition coefficients increase with increasing temperature at both constant oxygen fugacity and at constant redox buffer, we think it is important to try an alternative extrapolation for comparison. We have computed high temperature metal/silicate partition coefficients under a different set of assumptions and show that such long temperature extrapolations yield values which are critically dependent upon the presumed chemical behavior of the siderophile elements in the system.

Murthy's formulation starts from the following chemical potential equation:

 $\mu_i$  (metal) =  $\mu_i$  (silicate melt),

where i is the element of interest. We have interpreted Murthy's formulation to imply the following equilibrium partitioning reaction:

i(metal) = i(silicate melt)

However, this equilibrium does not take into account the change in valence of i on passing between metal and silicate melt and is therefore strictly valid only if the siderophile element is present in the same valence state in both phases. While there is some suggestion that Ni in silicate melts at low oxygen fugacity may in fact exist as a zero valence species (Colson, 1990; Morse et al., 1991), other elements such as P, W etc. are manifestly not present in the same valence states in metal and silicate melt, at least at low temperatures (Rammensee and Wänke, 1977; Newsom and Drake, 1983; Drake et al., 1984; Schmitt et al., 1989). Murthy expanded his chemical potential expression into activity and standard state terms and then selected experimentally-determined partition coefficients for each element at a single temperature to calculate  $\Delta\mu^0$  for the partitioning reaction at that temperature. Murthy used the calculated  $\Delta\mu^0$  to extrapolate partition coefficients for higher temperatures. However, Murthy's method implicitly assumes that  $\Delta\mu^0$  is not a function of temperature (see also Murthy, 1991b).

The thermodynamic approach used here is based on the heterogeneous oxidation/reduction reaction of siderophile elements in a two phase metal/silicate system. This method explicitly accounts for the change in valence of the partitioning species and uses experimental partition coefficients at more than one temperature to extrapolate to higher temperatures. For a siderophile element, i, the chemical reaction which we assume is responsible for the measured D<sub>met/sil</sub>'s is:

$$iO_{y/2}$$
 (silicate melt) =  $i^o$  (metal) +  $\frac{y}{4}O_2$  (silicate melt)

Our procedure assumes that the above chemical equation is valid over the temperature range of interest. The pertinent chemical potential equation explicitly incorporates the oxygen fugacity of the melt as shown below.

 $\mu_{iO_{y/2}}$  (silicate melt) =  $\mu_{i0}$  (metal) +  $\frac{y}{4}\mu_{O_2}$  (silicate melt)

If partition coefficients have been measured as a function of oxygen fugacity for, at least, two temperatures, we can utilize the van't Hoff relation for the temperature dependence of equilibrium constants to obtain an estimate of the partition coefficient at high temperature.

That it appears to be practically free of contamination from ITE-rich materials presumably derived from basin impacts suggests that it was an ancient, upper-level crustal component. The compositional similarities to components in lunar highlands meteorites [5,9] further suggests a widespread occurrence of ferroan, mafic (e.g., 10-15% pyroxene) igneous rocks.

Compositions of coexisting minerals from 67513 particles appear to form a related series covering an interval in the latter stages of magmatic crystallization (Plag + Pig -> Plag + Pig + Aug -> ilmenite saturation). Plots of molar Mg/(Mg+Fe) of mafic minerals and coexisting plagioclase form diagonally disposed groups on Fig. 3. To better resolve the igneous trends, only low-Ca pyroxene is plotted, and recombined bulk pyroxene compositions are plotted wherever possible. Two groups labelled A and B are apparent: group A contains the more pyroxene-rich fragments and group B, the more plagioclase-rich fragments. Members of group A are also related by similar compositions of trace chromite which occurs in most samples. These two groups may correlate to the "mafic ferroan" and "anorthositic ferroan" subgroups of [2]; the trend of group B parallels that shown for subsamples of 60025 by [1]. In one sample that contains zoned cumulus crystals, compositions of the most magnesian minerals and the most anorthitic plagioclase plot along extrapolations of trend B and the most ferroan mafic minerals coupled with the least anorthitic plagioclase plot within trend A. This is the effect of closed-system, fractional crystallization of trapped liquid [3] and provides a link between the two groups. The REE concentrations of fragments along trend A increase over an order of magnitude, reflecting the progressive incorporation of evolved liquid.

These two fractionation trends can be interpreted in the context of the broader model detailed by [3, also 1,2,10] wherein the near vertical trend requires equilibrium (adcumulus) crystallization of suspended plagioclase, and most of the mafic mineral components result from crystallization of trapped liquid (no cumulus pyroxene). The fractionation reflected by trend A results from combined crystallization of plagioclase and pyroxene cumulus crystals coupled with closed-system trapped liquid crystallization, but Mg' of mafic crystals is somewhat buffered by the presence of cumulus mafic crystals. Fractional crystallization of trapped liquid (closed system) leads to trends of even lower slope and is observed in one of the samples by comparing the most "evolved" pyroxene and plagioclase compositions of coarse crystal rims and fine-grained, interstitial crystals (Fig. 3, trend C).

Lunar rocks of the ferroan-anorthositic suite are commonly thought to have crystallized from a deep, crustal magma ocean [e.g., 11]. The mineral compositions and assemblages of the igneous fragments from 67513 require magmas whose Ca/Al ratios evolved to near chondritic values or greater. This requires extensive fractional crystallization if the parent magma was initially strongly subchondritic as has been argued for magma ocean compositions to account for observed anorthositic troctolitic, and noritic assemblages [3]. Crystallization modelling indicates that some 50% of a batch of magma must crystallize for mineral compositions to traverse trend A. The ITE enrichments of compositions at the evolved end of the trend require substantial trapped liquid fractions; fractional crystallization alone is insufficient to enrich cumulus minerals to the necessary degree.

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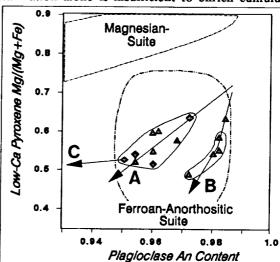


Figure 3. Plag An vs. low-Ca Px (Mg/Mg+Fe) in 67513 high Sc/Sm samples. Diamonds: bulk pigeonite; triangles: lamellae & separate crystals.

Estimation of High Temperature Metal-Silicate Partition Coefficients Jones, Capobianco, Drake

$$\ln D(T)_{\text{met./sil.}} = \ln K|_{T_2} + \left[\frac{1}{T} - \frac{1}{T_2}\right] \left[\frac{\Delta \ln K}{\Delta(\frac{1}{T})}\right]_{T_1, T_2} - \frac{y}{4} \ln f_{O_2}|_{T}$$

In the above equation D is the temperature-dependent metal/silicate partition coefficient, K is the equilibrium constant for the reaction,  $T_1$  and  $T_2$  are temperatures at which partition coefficients have been measured and for which the temperature derivative of lnK is calculated, and T is the new temperature of interest. In this approximation  $D_{\text{met/sil}}$  equals the mole fraction ratio of i in the metal and silicate. We have also implicitly assumed that the changes in silicate liquid composition between the experiments at different T's have not significantly affected the activity of i in the the silicate liquid.

We note that in general, at constant  $f_{O2}$ ,  $D_{met/sil}$  increases with increasing temperature. In other words, the experimentally-derived temperature dependence of most  $D_{met/sil}$ 's show increasing siderophility with increasing temperature. This is consistent with the chemical notion that oxides tend to dissociate at high temperatures and with the thermodynamic reasoning that high temperature favors the high entropy side of a reaction. The  $D_{met/sil}$ 's in Table 1 are reported for 3500K and  $f_{O2} = 10^{-3.2}$  (about IW-2 for 3500K) and Murthy's values are shown for comparison. Figure 1 plots log  $D_{met/sil}$  vs. log  $f_{O2}$  for elements in Table 1 to show how large  $f_{O2}$  effects can

suppress the effect of increasing temperature, especially for cations of high valence.

It should be noted that the calculated high temperature partition coefficients are highly sensitive to the details of the input experimental data, and different results are obtained from different published works for the same element. For example, using the published best fit coefficients for the logD vs. logf<sub>O2</sub> regressions through isothermal experimental data, one finds that extrapolated high-temperature partition coefficients are very sensitive to minor differences between the regression coefficients at T<sub>1</sub> and T<sub>2</sub> as shown in Figure 2. To obtain a consistent set of extrapolated D's, as shown in Figure 1 and Table 1 we have calculated new regression lines where necessary which force strictly temperature independent valences, corresponding to the most probable effective valence indicated by the experimental data. We do not find the experimental database sufficiently numerous to attempt to account for possible temperature-induced valence changes. However, there is no assurance that valences at high temperatures (and pressures) will be the same as those at low temperatures.

We conclude that, at present, it is not possible to extrapolate existing low temperature partition coefficients to yield meaningful high temperature estimates. Nevertheless, it appears likely that at least some high temperature metal/silicate partition coefficients will have significant values, and the magnitude of these values may be enhanced if light elements such as S are present. It seems premature to conclude that the "excess siderophile element" problem of the Earth's mantle is consistent with metal/silicate equilibrium at high temperatures and pressures. Direct experimental measurements are required.

Table 1. Calculated Liquid Metal/Silicate Liquid Partition Coefficients for 3500K and 1 bar† extrapolated from experimental data at lower temperature by Murthy (1991a) and this work.

	Input Data	P	Ga	W	Ge	Мо
Murthy		13	3.5	8.9	28.3	41.6
This work	Schmitt et al.	4	9	-	2700	-
This work	Drake Group	210,000	220	-	-	-
This work	Rammensee	-	1100*	120	-	$2.6 \times 10^6$
This work	Jones unpublished‡	5.6x10 <sup>7</sup>	-	1.9x10 <sup>10</sup>		

Assumed valences: P=5, Ga=3, \*Ga=1.3, W=4, Ge=2, Mo=4. †These D's are fictive in the sense that 3500K is above the boiling point of all major oxides except MgO at 1 bar. ‡solid metal/S-bearing silicate liquid partition coefficients

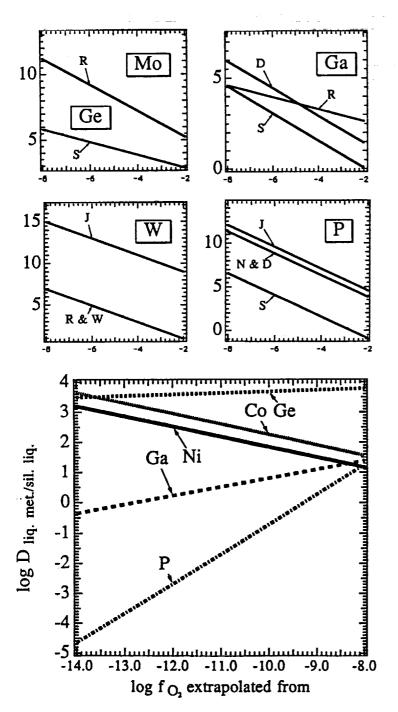


Figure 1. LogD<sub>met/sil.</sub> at 3500K and 1 bar vs. logf<sub>O 2</sub>. Orders of magnitude variations are observed for elements of high effective valence. Note that for Ga and P, for which multiple logD<sub>met/sil.</sub> estimates have been made, the agreement at 3500K is not good even though there is substantial agreement between independent data sets at 1573K. J=Jones unpublished; D=Drake et al. (1984); R=Rammensee (1978);S=Schmitt et al. (1989); R & W= Rammensee and Wänke (1977); N & D=Newsom and Drake (1983).

Figure 2. LogD<sub>met/sil.</sub> at 3500K and 1 bar vs. the logf<sub>O2</sub> at which the extrapolation was made. The input data are from Table 4 of Schmitt et al. (1989) and have been used directly as reported, except for the 1300°C data set for P which has been corrected for liquid metal/solid metal effects (see Murthy, 1991a). The cause for the extreme variation is due to changes in the experimentally-determined slopes on logD vs. logf<sub>O2</sub> plots between different temperatures. The data in Figure 1 are not dependent on the input oxygen fugacity because the available experimental data have been refitted to give temperature independent slopes on logD vs. logf<sub>O2</sub> plots.

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Mg-PEROVSKITE/SILICATE MELT PARTITION COEFFICIENTS IN THE CMS SYSTEM AT 2430°C AND 226 KBARS; Elisabeth A. McFarlane\*, Michael J. Drake\*, and Tibor Gasparik#. \*Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721, U.S.A; #Department of Earth and Space Sciences, SUNY Stony Brook, Stony Brook, New York 11794, U.S.A.

## INTRODUCTION:

The partitioning of elements amongst lower mantle phases and silicate melts is of interest in unraveling the early thermal history of the Earth (Kato et al., 1988a). Because of the technical difficulty in carrying out such measurements, only one direct set of measurements has been reported (Kato et al., 1988b), and these results as well as interpretations based on them have generated controversy (Walker and Agee, 1989). Here we report what are to our knowledge the first set of direct measurements on a synthetic system in the CaO-MgO-SiO<sub>2</sub> (CMS). A companion abstract reports on parallel experiments in the natural KLB-1 system (Drake et al., 1991).

## **EXPERIMENTAL:**

An experiment was conducted at Stony Brook using the USSA-2000 spilt sphere anvil apparatus. Reported here is an experiment in the CMS system doped with oxides of Al, Ti, Sc, and Sm and run at a nominal temperature of 2380°C and pressure of 226 kbars. Nominal temperatures were measured with a W3%Re/W25%Re thermocouple. The hot spot temperature, where the liquidus is located, is estimated to be at 2430°C. A 10mm MgO octahedron was used in concert with 4mm truncation edge lengths on the WC cubes. The sample was contained in a Re capsule which was inserted into a LaCrO<sub>3</sub> furnace. Pressure was calibrated at 2000°C. Run duration was approximately 3 minutes. The apparatus and experimental technique are described more fully in Gasparik (1990).

## ANALYTICAL:

The charge was mounted in epoxy and analyzed using a CAMECA SX-50 electron microprobe. Standard operating conditions were employed, although counting time for the less abundant elements was increased to improve counting statistics. The melt is unquenchable, and forms a dendritic intergrowth of quench crystals and residual melt. It was analyzed using a 30µm raster. The structural identity of the Mg-perovskite phase was confirmed using X-ray microdiffractometry at Universität Bayreuth.

#### **RESULTS:**

Mg-perovskite/silicate melt partition coefficients are given in the Table 1, along with the results of other workers. Partition coefficients for Mg, Al, and Si are similar to those of Kato et al. (1988b) except for Ti, and deviate less from unity than those of Drake et al. (1991). They also agree reasonably well for Ca, Sc, and Sm where other workers have reported results previously

Walker and Agee (1989) have pointed out that the temperature gradient in charges such as reported here can lead to thermal (Soret) diffusion in the silicate melt, raising questions concerning whether even a close approach to equilibrium was achieved. Because the melt does not quench to a glass, it is not possible to conduct a careful traverse away from the liquidus at the few micrometer scale (the effective spatial resolution of conventional electron microanalysis).

However, using a 30µm raster, stepping away from the liquidus boundary yielded no evidence of compositional gradients. This observation does not rule out Soret effects operating on a smaller spatial scale. However, we note that, in this experiment, the liquidus is located in the hot spot where temperature gradients are minimized.

MAGMA OCEAN: MECHANISMS OF FORMATION; W. M. Kaula, Dept. Earth and Space Sciences, University of California, Los Angeles CA 90024-1567

The thermal state of the Earth at the time relevant to formation of a magma ocean was dominated by the great impact that created the Moon. As shown in computer experiments, the iron in the impacting bodies quickly sank to the core of the proto-Earth, while a significant fraction of silicates was pushed far enough out beyond the geosynchronous limit to constitute the main material of the Moon. Most of any atmosphere would have been pushed aside, rather than being expelled in the impact.

However, the energy remaining in the material not going to the core or expelled was still sufficient to raise its temperature some 1000's of degrees, enough to vaporize silicates and to generate a strong "planetary wind": a hydrodynamic expansion carrying with it virtually all volatiles plus appreciable silicates. This expansion was violent and uneven in its most energetic stage, but probably the resulting magma ocean was global. The duration until cooling was sufficient for silicates to condense to melt was probably short.

Comparison of the Earth and Venus indicates that the great impact was extraordinarily effective in removing volatiles from the proto-Earth: in particular, the enormous differences in primordial inert gases between the planets—a factor of 80 in argon—demand a catastrophic difference in origin circumstances. But, on the other hand, the comparison limits the amount of silicates lost by the Earth to a rather minor fraction; most of that expelled in the wind must have condensed soon enough for the silicate to fall back to Earth or be swept up by the proto-Moon.

So the Earth was left with a magma ocean. The question is whether sufficient water was retained to constitute a steam atmosphere. Probably not, but unknowns affecting this question are the efficiencies of outgassing in great impacts and in subsequent convective churnings deep in the mantle. During the stage when mantle convection is turbulent, an appreciable fraction of volatiles would have been retained. Perhaps in the subsequent "lock-up" stage enough water would have escaped to make the oceans, but the puzzling failure of lock-up to stratify the mantle in silicates suggests that appreciable volatiles were also retained at depth, perhaps in some mineral phases not yet well-defined. We still have primordial helium being outgassed.

An important constraint from the great Venus: Earth differences in primordial inert gases is that there could not have been much delivery of volatiles from the outer solar system after the great impact.

## **DISCUSSION:**

There has been a significant debate concerning whether measured values of trace element partition coefficients permit large scale fractionation of liquidus phases from an early terrestrial magma ocean (Kato et al., 1988a,b; Walker and Agee, 1989; Drake, 1989; Drake et al. 1991; McFarlane et al., 1990, 1991). Taken in isolation, our results do not appear to be consistent with large scale fraction of Mg-perovskite from an early ocean, because approximately chondritic ratios of refractory lithophile elements inferred for the primitive upper mantle of the Earth would be destroyed (Figure 1). However, it should be noted that it is unclear which, if any, numerical values of partition coefficients in Table 1 is appropriate, and fractionation of other phases has not been considered.

TABLE 1. Mg-Perovskite/Melt Partition Coefficients

	This Work 226 kbar 2430°C measured	Kato, 88a 250 kbar 2000°C calculated	Kato, '88b 250 kbar 2000°C measured	Drake, '91 250 kbar 2400°C measured
Mg	1.0	•	•	0.8
Al	1.2	0.5	1.3	2.3
Si	1.1	*	*	1.9
Ca	0.2	0.2	0.1	0.7
Ti	0.6	3	1.3	
Sc	1.6	5	2.8	*
Sm	0.2	0.3	<0.2	*

<sup>\*</sup> not measured

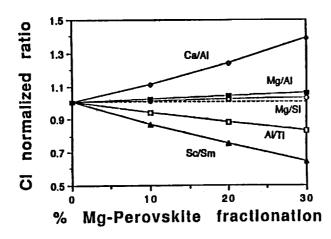


Figure 1. The variation of various element ratios that would be observed in the upper mantle of the Earth with the fractionation of magnesium perovskite from a melt, such as might have occurred during a postulated magma ocean stage. Magnesium perovskite formation and sinking would result in significant fractionation of refractory lithophile elements away from the approximately chondritic ratios which are observed in the primitive upper mantle.

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FATE OF A PERCHED CRYSTAL LAYER IN A MAGMA OCEAN, S. A. Morse, Geol/Geog., UMass, Amherst MA 01003 USA.

The pressure gradients and liquid compressibilities of deep magma oceans should sustain the internal flotation of native crystals owing to a density crossover between crystal and liquid; olivine at upper mantle depths near 250 km (1-3) is considered here. The behavior of a perched crystal layer is part of the general question concerning the fate of any transient crystal carried away from a cooling surface, whether this be a planetary surface or the roof of an intrusive magma body. For magma bodies thicker than a few hundred meters at modest crustal depths, the major cooling surface is the roof even when most solidification occurs at the floor. Importation of cool surroundings must also be invoked for the generation of a perched crystal layer in a magma ocean, but in this case the perched layer is deeply embedded in the hot part of the magma body, and far away from any cooling surface. Will the crystal layer survive? Probably not, but its ephemeral presence is still important.

Assume two cooling surfaces to the magma ocean (MO), with an upper radiation rate much greater than the conduction rate into cold rock below. Impacts, crystal phase changes, crust formation and melting interval are ignored for the present. Assume two thermal gradients, a steeper T<sub>1</sub> for the liquidus and an adiabatic T<sub>MO</sub> for the magma ocean. Internally driven thermal turbulence is ignored because of crystallization at the surface of the magma ocean, which will tend to maintain a transient conductive lid, and because of the vigorous operation of two-phase convection (4,5), which will tend to override thermal turbulence. The *liquidus* temperature is here assumed to be equal to the solidus temperature at any depth; solidification occurs without change of composition, hence isothermally (but see later). Crystals will be transported in two-phase (S + L) plumes to the neutral point in the density contrast; these plumes will be downwarddirected (negatively buoyant) in the upper cell and upward directed (buoyant) in the lower cell, where upper and lower are defined with reference to the neutral point. Nuclei are not expected in the lower cell, however. In the chief case of interest, the liquidus temperature increases monotonically to the base of the magma ocean, which is adiabatic except near the surface thermal boundary layer. Crystals nucleate near the ocean surface and are carried downward in cold two-phase plumes. They come to rest at the neutral point, but they can survive only if the cold plumes keep arriving fast enough. In this case, a suspension cumulate is formed, and its persistence cools the magma ocean locally, causing a thermal pucker. The cumulate layer melts at its lower surface but accretes at the upper surface faster than melting can take place (if we want to have a solid layer). No action occurs within the lower cell. The upper cell supports "PT cycles" (6) in which cold plumes flow downward and the upward-flowing return plumes carry away the latent heat of crystallization released from the cumulate. The temperature of the magma ocean is locked to the equilibrium (S + L) temperature throughout the cumulate suspension, wherever crystals coexist with liquid (Fig. 1). The base of the crystal layer is forever melting because the magma ocean in the lower cell is hot. Addition of more crystals at the upper cumulate surface depresses the base of the layer and embeds it into hotter magma, so it melts faster. The crystal layer thereby acts as a heat pump in which heat is extracted from the lower cell by melting and added to the upper cell by crystallization. The condition will remain like that in Fig. 1 until a durable crystalline

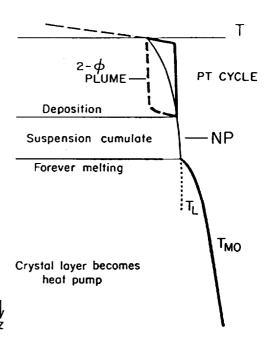
lid is established at the planetary surface. As soon as this occurs, cooling becomes dominated by conduction; the perched crystal layer can no longer be fed faster than it melts, and it will disappear.

Assuming continued buoyancy of the liquidus phase at the NP, cold two-phase plumes will continue to deliver crystals to the NP, where they instantly melt, acting as a heat absorber for the lower cell. This must in fact be the principal mode of heat loss from the lower cell. The last liquid disappears at or near the neutral point, which becomes the base of the lithospheric lid. The entire mantle below the NP remains at a high value of the homologous temperature; it is therefore ductile, the original asthenosphere. Adiabatic upwelling will now give rise to copious magmatism due to decompression melting. Because of melting at the lower surface of the perched olivine layer, the lower cell becomes more olivine rich. Therefore the original olivine richness of the upper mantle should be concentrated below 250 km but above the transition zone. If the base of the crystal layer undergoes partial melting, the more iron-rich partial melt will probably drain downward. The lower cell should, therefore, become more iron rich and the crystals more buoyant than in the original magma ocean. The partial melting process might lead to a very refractory crystal residue near NP, and that could become thermally stable owing to its higher solidus; the perched layer would cease to be ephemeral. However, it would still have to transfer heat from the lower cell, so would probably remain porous (7). The bottom line is that the NP acts as a staging area where material and heat transfer take place. The NP probably becomes the base of the rigid lithospheric lid and the upper bound of the asthenosphere. Can we see this effect? Yes, very likely in that the upper mantle seems to be more olivine rich than the bulk mantle, as noted by many workers.

Fig. 1

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EVIDENCE FOR A HIGH TEMPERATURE DIFFERENTIATION IN A MOLTEN EARTH: A PRELIMINARY APPRAISAL. V. Rama Murthy, Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455.

If the earth were molten during its later stages of accretion as indicated by the present understanding of planetary accretion process (1), the differentiation that led to the formation of the core and mantle must have occurred at high temperatures in the range of 3000-5000 K because of the effect of pressure on the temperature of melting in the interior of the earth. This calls into question the use of low-temperature laboratory measurements of partition coefficients of trace elements to make inferences about earth accretion and differentiation (2). The low temperature partition coefficients cannot be directly applied to high temperature fractionations because partition coefficients refer to an equilibrium specific to a temperature for a given reaction, and must change in some proportion to exp 1/RT. There are no laboratory data on partition coefficients at the high temperatures relevant to differentiation in the interior of the earth, and an attempt to estimate high temperature distribution coefficients of siderophile elements was made (3) by considering the chemical potential of a given element at equilibrium and how this potential changes with temperature, under some specific assumptions. Since  $\Delta\mu^o$ for the metal-silicate partition was determined from laboratory measurements at T<sub>1</sub> and held constant in the extrapolations to high temperature  $T_2$ , whereas in actuality  $\Delta\mu^0$  also changes with T, this is not a rigorous solution. Rigorously,  $\Delta\mu^{o}$  at T<sub>2</sub> requires a knowledge of  $\Delta S_{r}$ and  $\Delta V_r$ , which are not known, but most likely have have opposite effects. Nevertheless, or perhaps because of this combined but opposite effects of  $\Delta S_r$  and  $\Delta V_r$  terms in the deep earth, an interesting outcome of this exercise was that it seemed to provide a reasonably satisfactory explanation of the observed siderophile abundances in the mantle, resolving a long-standing geochemical enigma which has inspired exploration of many creative and complex models of earth's accretion and differentiation (e.g. 4, 5).

A molten earth implies that the molten silicate mantle solidified subsequently and so must exhibit elemental fractionations which should be particularly noticeable in the trace element ratios of elements with partition coefficients >1 and < 1, due to crystal-liquid separations in the magma ocean. Whether the geochemical evidence from the mantle is in accord with such a scenario is unresolved at present. From phase equilibrium studies and mass balance considerations, Agee and Walker (6) have deduced that about 27% Mg-perovskite fractionated into the lower mantle and that due to the pressure-density relations in the mantle, about 30% of olivine is added to the upper mantle. Extrapolating the partition coefficients of some lithophile elements to high temperatures as done for the siderophile element fractionation (3), the expected abundances in the upper mantle have been derived by using Rayleigh fractionation systematics and compared in Fig.1 to those observed in the upper mantle (5). The agreement between the calculated ratios and those observed is hard to ignore, especially noting that the agreement is about ± 10% for the trace element ratios and ± 20% for the major element ratios. This is remarkable considering the uncertainties of the estimates for the upper mantle, the fairly large uncertainties of the experimental measurements and the fuzziness in the extrapolation of the partition coefficients to high temperatures as done here. Other phases, such as Mg-wustite and majorite garnet may have played a role in the elemental fractionations discussed above. However, for a chondritic composition, phase-equilibria studies show that the relative abundances of these phases are quite small relative to Mg-perovskite. Rather than using the Mgperovskite/liquid distribution coefficients, a bulk distribution coefficient representative of a solid composed of these phases can equally well be employed, but it can be readily shown that this will not materially alter the agreement between the calculated and observed abundances shown in Fig.1. Also, rather than use Rayleigh fractionation systematics, which may or may

not be appropriate at high temperatures, mass balance methods might be used, but once again, the match between the calculated and observed abundances remains excellent. Olivine addition by flotation into the upper mantle (6) affects the Sc/Sm and Mg/Si ratios and brings both these ratios to a close agreement with the observed values. The high Mg/Si ratio relative to chondritic meteorites may thus be due to magma ocean fractionations rather than due to cosmo-chemical fractionations.

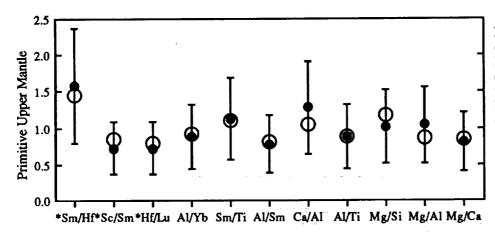


Fig. 1. Calculated ratios (solid circles) for a 27% Mg-Pvsk. fractionation compared to observed values (open circles). Error bars ±50% are estimated errors in the measured partition coefficients. The ratios with \* have been cited as evidence against the magma ocean concept.

Thus, it appears that a high-temperature differentiation in a molten earth, no matter how crudely evaluated in this approach, can reasonably well account for both the siderophile elements in the mantle established after core segregation and the lithophile element characteristics of the upper mantle, caused by crystal-liquid fractionations during the solidification of a global magma ocean. The overall geochemical evidence thus seems supportive of the recent quantitative theories of planetary accretion which require an initially molten earth. The concept that element fractionations in a planetary body are characteristic of its size-dependent internal temperature may prove helpful in understanding the early differentiation and evolution of other planetary bodies as well.

Jones et al. (7) have presented an alternative thermodynamic approach by considering the behavior of oxidation-reduction reactions and extrapolation to high temperature by the van't Hoff relationship. While my estimates of high T coefficients suffer from  $\Delta\mu^0$  being held constant, it is unclear how meaningful are the van't Hoff extrapolations when the  $\ln K \, \underline{vs} \, 1/T$  relationship is determined over a small range of T and by very few experimental points. The important point to note, and one to which not much attention has been given before, is that the temperature of differentiation in the interior might be a relevant factor in understanding earth accretion and differentiation. Experimental data that bear on this point directly are needed.

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FORSTERITE/MELT PARTITIONING OF ARGON AND IODINE: IMPLICATIONS FOR ATMOSPHERE FORMATION BY OUTGASSING OF AN EARLY MARTIAN MAGMA OCEAN; Donald S. Musselwhite, Michael J. Drake, and Timothy D. Swindle, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721

## INTRODUCTION:

Argon and Xe in the martian atmosphere are radiogenic relative to the martian mantle (Table 1) if the SNC meteorites are from Mars [1]. Decay of the short lived isotope  $^{129}$ I to  $^{129}$ Xe ( $t_{1/2} = 16$  m.y.) is the most plausible source of the radiogenic Xe. This short half life constrains any process responsible for the elevated  $^{129}$ Xe/ $^{132}$ Xe ratio of the martian atmosphere to occur very early in solar system history. Musselwhite *et al.* [2] proposed that the differential solubility of I and Xe in liquid water played a key role in producing the radiogenic signature in the martian atmosphere. Here we explore an alternative hypothesis involving purely igneous processes, motivated in part by new experimental results on the partitioning of I and Xe between minerals and melt.

## ARGON AND IODINE PARTITIONING EXPERIMENTS:

Previous experimental approaches have been designed around the necessity of separating crystal and glass to permit analysis of pure phases by noble gas mass spectrometry [3,4]. Our approach eliminates the need for phase separation because higher concentrations are attained in the

various phases allowing in situ microprobe analysis.

Experiments investigating Ar solubility in silica glass [5] revealed that an Ar concentration of 2 wt. % can be attained in the silica glass under 2 to 4 kbars Ar pressure. We utilize this observation to introduce Ar into our charges. Finely crushed silica glass in a loosely crimped but not gas tight platinum capsule is placed in a gas pressure vessel and subjected to 2 kbars of Ar at 400°C for 48 hours. The Ar-bearing silica glass plus KI are then used to prepare starting material in the CAMS system [6]. The charges are run in a piston-cylinder apparatus at a temperature and pressure appropriate to yield  $\approx 20\%$  crystals. The quenched run products are mounted in epoxy and analyzed by a CAMECA SX-50 electron microprobe. Argon is calibrated by interpolating intensities of adjacent elements [7]. In this manner D(I) and D(Ar) can be determined simultaneously and, from D(Ar), D(Xe) can be estimated [3,4]. A preliminary forsterite/melt experiment at 15 kbars and 1480°C yields D(Ar) < 0.05 and D(I) = 0.001.

## MINERAL/MELT PARTITIONING FOR XE:

Mineral/melt partitioning experiments [3,4] show that light noble gases are always less compatible in the crystals than heavy species. Precise numerical values of noble gas partition coefficients are uncertain, however. For example, experimentally determined values for D(Xe) vary from 0.05 to >> 1, and it is unclear which of the values are geologically significant. Particularly important is the question of whether D(Xe) is greater than or less than unity.

Our simultaneous determination of a forsterite/melt D(Ar) and D(I) allows us to predict an internally consistent D(Xe) from the trends seen by other investigators. Using the ratio of D(Xe)/D(Ar) ratio = 13.4 from [4] we predict D(Xe) < 0.7 and using the D(Xe)/D(Ar) ratio = 2.3 from [3] we obtain an upper limit for D(Xe) < 0.1. These estimates are consistent with [3] who reported a range of 0.15 - 0.5 for D(Xe). These results lead us to the conclusion that I/Xe ratio would be increased in a melt relative to the crystal phases during crystallization of a magma ocean. The results also suggest that Xe is not compatible in forsterite as had been permitted by some experimental results [4].

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## **OUTGASSING OF A MARTIAN MAGMA OCEAN:**

The greater compatibility of Xe relative to I in forsterite, if true of other mantle mineral phases, points to producing the radiogenic Xe in the martian atmosphere by multistage outgassing of the martian mantle: 1) During crystallization of a martian magma ocean, crystal/melt partitioning increases I/Xe ratio and total abundances of I and Xe in the residual melt, the magnitude of the increases depending on the degree of partial melting responsible for creating the magma ocean and the degree of crystallization. Crystalline phases have smaller I/Xe ratios and lower total abundances. 2) Outgassing of the magma ocean to an early atmosphere, if very efficient (≈ 95%), will lower the total I and Xe abundances and further enhance the I/Xe ratio in the magma. 3) <sup>129</sup>I decays to <sup>129</sup>Xe in the magma ocean. 4) Volatiles outgassed from the magma ocean in the first 0.5 Ga of Mars history are removed from the atmosphere by impact erosion during late accretion and heavy bombardment [8]. 5) Subsequent outgassing of the magma ocean reservoir yields a radiogenic Xe signature in the martian atmosphere. Radiogenic Ar from K decay is also released. 6) SNC basalts are derived from the nonradiogenic cumulates produced from the earliest crystallization of the magma ocean.

## **CONCLUSIONS:**

This model differs from the water solubility fractionation model [2] in that later outgassing of the martian mantle serves as the radiogenic noble gas source for the atmosphere, rather than a surface or near surface reservoir of radiogenic noble gases due to sequestering of parent isotopes by liquid water. In both models the mantle outgasses in the first 0.5 Ga and the initial mantle-derived atmosphere is removed by impact erosion. The model presented here would also work with partial melting of a largely solid mantle rather than crystallization of a magma ocean. Note also that there are parallels between this model and the model for early outgassing of the Earth's MORB mantle source proposed by [9,10]. Our experimental result suggests that outgassing of the MORB source does not need to be as efficient as that for the martian atmosphere source. The difference in outcome for Mars results from atmospheric erosion of the martian atmosphere which has been shown not to occur on the Earth.

Table 1: 129Xe /132Xe and 40Ar /36Ar ratios in Mars Reservoirs11-13

	129 <sub>Xe</sub> /132 <sub>Xe</sub>	40Ar /36Ar
Atmosphere	2.5	3000
Basalts	1.0-1.5	230

#### Table 2: Mineral/Melt Partition Coefficients

<u>Iodine</u>			Argon*	<u>Xenon</u>		
,	1 Atm 1300°C4	15 Kb 1480°C*	15 Kb 1480°C	1 Atm 1300°C6,7	**	
Forsterite	≤0.04	0.001	<u>≤</u> 0.05	0.5 to 9	≤0.7 to 0.1	
	1	This work				

<sup>\*\*</sup> Estimated from D(Ar) this work and the D(Xe)/D(Ar) ratio from 6,7

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PRESSURE REGIMES AND CORE FORMATION IN THE ACCRETING EARTH; H.E. Newsom, Institute of Meteoritics and Department of Geology, University of New Mexico, Albuquerque NM 87131

Quantitative models of core formation that have been constructed to explain the abundances of siderophile elements in the Earth's mantle are currently based on metal-silicate partition coefficients determined at low pressures [1]. The varying pressure regimes during the accretion of the Earth, however, may dramatically affect the metalsilicate partition coefficients, placing constraints on the possible models. The development of magma oceans, due to large impacts or the effects of a blanketing atmosphere, is closely coupled with the need for large degrees of melting to segregate metal from silicates. Siderophile element models for the Earth can be easily divided into two classes of models, subtractive models, in which the observed depletions of siderophile elements in the mantle are established by equilibrium partitioning processes, and additive models, in which the abundances of siderophile elements are controlled by the addition of late veneers to a mantle that is highly depleted in siderophile elements. Both of these classes of models may be affected by metal-silicate partitioning at higher pressures and temperatures. At high pressures within the Earth, the stable mineral assemblage is different from the low pressure assemblage. Two pressures are of particular interest. In the present Earth, 15 GPa (150 kbar) is roughly the pressure of the 400 km depth phase transition from α-olivine and pyroxene to the denser β phase. 25 GPa (250 kbar) is roughly the pressure of the 675 km depth phase transition in the Earth where perovskite and magnesiowüstite forms from olivine and garnet. 25 GPa is also the pressure where oxygen becomes soluble in Fe-metal [2]. The partition coefficients for such a metal alloy may be quite different from an oxygen-free alloy, but siderophile element partition coefficients have not yet been reported for such pressures.

Recent work suggests that a large degree of melting is required to segregate metal from silicates, suggesting a connection with the formation of magma oceans [3]. At low pressures metallic liquids do not wet silicate minerals, preventing the metal from aggregating into large masses that can sink. At high pressures, above 25 GPa, the dihedral angles of grains in contact with oxygen-rich metallic liquids may be reduced enough to allow percolation of metal, but this has not been confirmed. Physical models of core formation and accretion may therefore involve the formation of magma oceans and the segregation of metal at both high and low pressures. I will discuss below models of core formation involving different pressure regimes, and then discuss some of the geophysical and chemical evidence bearing on the models.

High-pressure models: Models involving high-pressure metal-silicate equilibrium can involve the formation of deep magma oceans, or percolation of metallic liquids at high-pressures. For example, high-pressure effects dominate a model in which core formation is delayed until late in the accretion of the Earth, when an event, such as a giant impact, melts the Earth. Stevenson [3] has discussed the possibility of a metal-alloy segregating under high-pressure conditions from a viscous boundary layer at the base of such a magma ocean. This would correspond to a simple equilibrium siderophile element model if the high-pressure partition coefficients turn out to have the appropriate values.

A high pressure equilibrium siderophile signature could also result, assuming continuous core formation during accretion, if metal segregates at shallow depths, but reequilibrates with silicates at high pressure. Rapid convection during accretion would be necessary to transport upper mantle material to the lower mantle, where it can acquire a high pressure signature. Mantle material which accreted during the early low-pressure phase of accretion would also have to reequilibrate with metal-alloy at high pressures.

Core formation could also involve the percolation of metallic liquids at high pressures. This mechanism could be responsible for core formation without extensive melting if whole mantle convection carried newly accreted upper mantle material containing metal into the lower mantle, where the metal can segregate.

The heterogeneous accretion model (an additive model) assumes that most of the metal content of the Earth accreted by the time 80% to 90% of the Earth had accreted. During this first stage of accretion, the core formation process must result in significant depletion of the moderately siderophile elements below their present abundances. This could be consistent with high-pressure equilibration only if the high-pressure metal-silicate partition coefficients are large enough. For this model, compared to the homogeneous accretion of metal and silicate, the pressure environment for metal segregation will be somewhat higher on the average because of the rapid formation of the core. After accreting additional material to establish the abundance of the moderately siderophile elements, a second stage depletion is required, to lower the abundance of the highly siderophile elements (e.g. Pt, Ir, Au) below their

observed abundance, without significantly disturbing the abundances of the moderately siderophile elements (e.g. Co, 43 Ni, W). This second stage depletion could involve the segregation of metal or sulfides at high pressures, for example at the base of a magma ocean. The heterogeneous accretion model usually invokes the third stage accretion of a late veneer of material to bring in the highly siderophile elements in their chondritic relative abundances. If the high-pressure partition coefficients for the highly siderophile elements are similar and of the right absolute magnitude, the highly siderophile element signature could be the result of high-pressure equilibrium during the second stage depletion phase.

Low-pressure models: Models involving low-pressure metal-silicate equilibrium generally involve the formation of shallow magma oceans. During the initial stage of accretion, until the Earth's mass reaches 30% to 40% of its present mass, the pressures within the proto-earth will be relatively low, below 25 GPa. Core formation in the Earth probably occurred during this stage, based on the geophysical evidence for a core in the planet Mars (total mass 11% of Earth's) and the evidence pointing to the differentiation of asteroids in the inner solar system. In order to establish a low-pressure siderophile signature in the upper mantle, core formation must proceed in such a way that metal segregating at shallow depths cannot reequilibrate under high pressures. This could be accomplished, for example, by accumulation of metal from a shallow magma ocean into large masses, such that the metal will rapidly sink as large metallic diapirs through the lower mantle.

Another physical model is to infer a complete lack of communication between the lower mantle and the upper mantle since accretion, such that we have no sample of silicates that reequilibrated with metal at high pressures. Metal segregation within the upper mantle in this model could also involve a shallow magma ocean.

Quantitative siderophile element partitioning models that directly apply to these low-pressure scenarios have been discussed by Newsom [4]. The most successful models are heterogeneous accretion, and inefficient core formation, an equilibrium model involving retention of metal and sulfide in the mantle.

Mixed high- and low-pressure models: Because the high-pressure environment of the Earth's mantle is restricted to the later stages of accretion, and to the lower mantle, the siderophile element signature of the mantle is likely to record effects due to both high and low pressure partitioning. A simple homogeneous accretion model, with continuous core formation would result in early accreting mantle material that equilibrated with metal at low pressures. During the later stages of accretion, metal segregation in a deep magma ocean or percolation of metallic liquids at high pressures will begin to impart a high-pressure signature. Depending on factors such as the amount of convection and the depth of a magma ocean, the final siderophile element signature may reflect a mixture of signatures produced at high and low pressures.

A heterogeneous accretion model could also involve high- and low-pressure effects. During the first stage of accretion, involving 80% to 90% of the Earth's mass, the situation described in the previous paragraph will apply, with conditions at the base of the mantle going from low-pressure to high-pressure. During the second stage depletion, after most of the Earth has accreted, the metal segregation could occur either in a shallow magma ocean at low pressure, or in a deeper magma ocean with the possibility of high pressure effects. Even more complicated accretion and core formation models can be envisioned [e.g. 5], but the resulting siderophile element signatures are likely to be non-unique.

Discussion: Unfortunately, current evidence does not allow us to discard any of the above models. Available geophysical data is ambiguous. The nature of the 670 km boundary (chemical difference or strictly phase change) between the upper and lower mantle is in doubt. There is some evidence that plumes are derived from the lower mantle, and seismic tomography strongly indicates penetration of subducting oceanic crust into the lower mantle, but the tomography data also indicates that the 670 km discontinuity is a significant barrier to general mantle convection. The presence of the D" layer at the base of the lower mantle could be a reaction zone between the mantle and core indicating core-mantle disequilibrium, or the D" layer could be subducted material. The abundance of the siderophile elements in the mantle could provide clues to the importance of high pressure processes in the Earth, but partition coefficients at high pressures are only beginning to be measured.

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TERRESTRIAL MAGMA OCEAN AND CORE SEGREGATION IN THE EARTH Eiji Ohtani, Institute of Mineralogy, Petrology, and Economic Geology, Tohoku University, Sendai, Japan.

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According to the recent theories of formation of the earth, the outer layer of the proto-earth was molten and the terrestrial magma ocean was formed when its radius exceeded 3000 km (1, 2). Core formation should have started in this magma ocean stage, since segregation of metallic iron occurs effectively by melting of the proto-earth. Therefore, interactions between magma, mantle minerals, and metallic iron in the magma ocean stage controlled the gechemistry of the mantle and core.

We have studied the partitioning behaviors of elements into the silicate melt, high pressure minerals, and metallic iron under the deep upper mantle and lower mantle conditions. We employed the multi-anvil apparatus for preparing the equilibrating samples in the ranges from 16 to 27 GPa and 1700-2400 °C. Both the electron probe microanalyser (EPMA) and the Secondary Ion Mass spectrometer (SIMS) were used for analysing the run products. We obtained the partition coefficients of various trace elements between majorite, Mg-perovskite, and liquid, and magnesiowustite, Mg-perovskite, and metallic iron. The examples of the partition coefficients of some key elements are summarized in figures 1 and 2, together with the previous data (3).

We may be able to assess the origin of the mantle abundances of the elements such as transition metals by using the partitioning data obtained above. The mantle abundances of some transition metals expected by the core-mantle equilibrium under the lower mantle conditions can not explain the observed abundance of some elements such as Mn and Ge in the mantle (4).

Estimation of the densities of the ultabasic magma and Mg-perovskite at high pressure suggests existence of a density crossover in the deep lower mantle; flotation of Mg-perovskite occurs in the deep magma ocean under the lower mantle conditions (5, 6, 7).

The observed depletion of some transition metals such as V, Cr, Mn, Fe, Co, and Ni in the mantle may be explained by the two stage process, the core-mantle separation after core-mantle equilibrium under the lower mantle conditions in the first stage, and subsequent downwards separation of the ultrabasic liquid (and magnesiowustite) and flotation of Mg-perovskite in the lower mantle. The segregated ultrabasic liquid (and magnesiowustite) from the lower mantle might have sunk into the core-mantle boundary. The D" layer at the base of the mantle and outer core might have been composed, at least, partly of such materials segregated in the primordial earth (8). Thus, the magma ocean with a partially molten zone extending into the deep lower mantle might have existed during the core formation

ESTIMATION OF THE VISCOSITIES OF SILICATE LIQUIDS AT HIGH PRESSURE FROM MEASUREMENTS OF OXYGEN DIFFUSIVITY

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The dynamics and evolution of a magma ocean depend significantly on the structure and physical properties of silicate liquids at high pressure. Viscosity is particularly important because of its effect on the dynamics of convection and crystal settling. Traditionally the viscosities of silicate liquids have been measured at high pressure by falling-sphere viscometry [1] but, due to some limitations of this technique, few measurements have been made at pressures exceeding 2.5 GPa. An alternative approach, which has previously been proven up to 2 GPa [2], is to use high-pressure measurements of oxygen self-diffusivity (D) to estimate viscosity ( $\eta$ ) from the Eyring relationship  $\eta = kT/D\lambda$  (where k is the Boltzmann constant, T is absolute temperature and  $\lambda$  is the diffusive jump distance). We have performed preliminary experiments on Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> liquid in order to explore the feasibility of this method up to pressures in excess of 10 GPa. Diffusion couples were prepared from glass starting materials with one half of the sample enriched in <sup>18</sup>O and the other half containing the natural abundance (0.2 wt%). Diffusion experiments were performed at 1600-1800 °C at pressures in the range 2.5-10 GPa for times up to 6 minutes using a 1200 ton multianvil apparatus. Oxygen diffusivities were derived from the resulting 18O concentration profiles, which were analyzed using an ion microprobe. At 1800 °C, oxygen diffusivities increase continuously from 1 x  $10^{-10}$  m<sup>2</sup> s<sup>-1</sup> at 2.5 GPa to 5 x  $10^{-10}$  m<sup>2</sup> s<sup>-1</sup> at 10 GPa. From the Eyring relationship the viscosity of Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> liquid is predicted to decrease by ~0.7 log units over this pressure range at 1800 °C. These trends, which can be related to changes in the structure of the liquid at high pressure, are in agreement with the results of molecular dynamics calculations [3]. These results suggest that it should be possible to estimate the viscosities of silicate liquids up to at least 15 GPa and 2200 C by this method.

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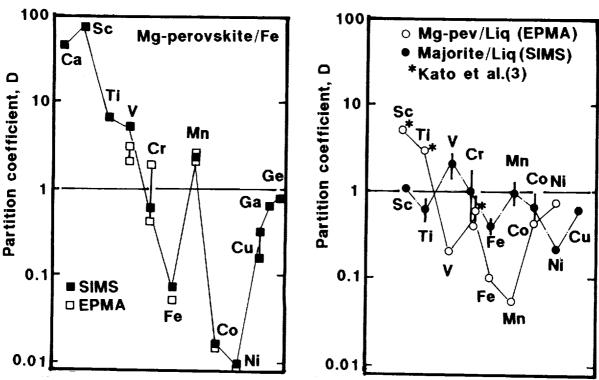
stage of the earth. The whole mantle was homogenized in the later stage due to the convective mixing by the early Archean (35-38 Ga), since recent data on Hf isotope of the Barberton komatilte show  $e_{\rm Hf}$  around zero, which indicates the chondritic source mantle in the early Archean in terms of the refractory lithophle elements such as Lu and Hf (9).

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Fig.1. Partitioning between Mg-pev and metallic iron

Fig.2. Partitioning between Majorite, Mg-pev and Liquid



COOLING OF THE MAGMA OCEAN DUE TO ACCRETIONAL DISRUPTION OF THE SURFACE INSULATING LAYER; Sho Sasaki, Department of Earth and Planetary Systems Sciences, Faculty of Science, Hiroshima University, Higashi-Hiroshima, 724 Japan

Planetary accretion has been considered as a process to heat planets. Some fraction of the kinetic energy of incoming planetesimals is trapped to heat the planetary interior [Kaula, 1979; Davies, 1984]. Moreover, blanketing effect of a primary atmosphere [Hayashi et al., 1979; Sasaki, 1990] or a degassed atmosphere [Abe and Matsui, 1986; Zahnle et al., 1988] would raise the surface temperature of the Earth-size planets to be higher than the melting temperature. The primordial magma ocean was likely to be formed during accretion of terrestrial planets.

In the magma ocean, if crystalized fractions were heavier than melt, they would sink. But if solidified materials were lighter than the melt like anorthosite of the lunar early crust, they would float to form a solid shell surrounding the planet. (In an icy satellite, solidified water ice should easily float on liquid water because of its small density.) The surface solid

lid would prevent efficient convective heat transfer and slow the interior cooling.

Consider that the accretion of planetesimals still continues in this cooling stage. Shock disruption at planetesimal impact events may destroy the solid insulating layer. Even if the layer survives impacts, the surface layer is finally overturned by Rayleigh-Taylor instability, since accreting materials containing metals are heavier than the surface solidified lid of silicates (Fig. 1).

The internal heat is escaped from the surface through the resolidification of the surface layer. Assuming that the disruption of the surface layer takes place once in an interval fint in average [Stevenson, 1989], we can write the heat loss per unit time as

$$L_{es} = 4\pi R^2 \delta \rho (C_p \Delta T + Q\phi) t_{int}^{-1}$$

where R is planetary radius,  $\rho$  is density,  $C_p$  is the specific heat,  $\kappa$  is the thermal diffusivity, Q is the latent heat of melting,  $\Delta T$  is temperature difference between the surface and the underlying magma ocean,  $\phi$  is melt fraction of the magma ocean, and  $\delta = (\xi \kappa t_{\text{int}})^{1/2}$  is the thickness of the solidified layer.

We may assume that area of impact craters is the area of the impact-induced disruption. We include its dependence on the planetary mass, assuming  $D \propto E^{1/3}$  (D and E being crater diameter and kinetic energy, respectively), which may reproduce experimental results. Normalizing by accretional heating rate  $L_{\rm ac} = GM\dot{M}(h+\alpha)/R$ , we finally have

$$\frac{L_{es}}{L_{ac}} = 1.1 \times \left(\frac{\dot{M}}{M_{\rm E}/10^9 \, \rm yr}\right)^{-\frac{1}{2}} \left(\frac{h+\alpha}{0.1}\right)^{-1} \left(\frac{M}{1 M_{\rm E}}\right)^{-\frac{1}{9}} \left(\frac{m_{eff}}{10^{18} \, \rm kg}\right)^{-\frac{1}{6}}$$

where M is planetary mass and M is mass accretion rate of planetesimals. Parameter h denotes mean energy fraction which is trapped as a heat at the impact event. And  $\alpha$  is the ratio of heating by metal-silicate (ice-rock) fractionation to the total accretional energy. And  $m_{\rm eff}$  is the effective mean size of accreting planetesimals. We estimate  $m_{\rm eff}$  taking into account mass distribution of planetesimals.

Even if the size of accreting planetesimals is small compared with the thickness of the surface layer and impact disruption of the surface layer is inefficient, accumulating materials are heavier than the solidified surface layer and cause overturn of the surface layer. In this

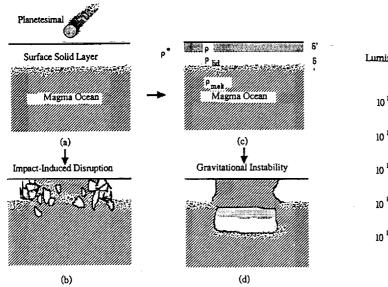
case we have the normalized cooling flux

$$\frac{L_{es}}{L_{ac}} = 1.6 \times \left(\frac{h+\alpha}{0.1}\right)^{-1} \left(\frac{M}{1M_{\rm E}}\right)^{-\frac{2}{3}}$$

where dependence on mass accretion rate is cancelled.

In Fig.2, energy loss by the surface layer disruption  $L_{\rm es}$  and the trapped accretion energy  $L_{\rm ac}$  are shown as functions of mass accretion rate. In the Rayleigh-Taylor instability case,  $L_{\rm es}$  is a little larger than  $L_{\rm ac}$  at any mass accretion rate. In the impact disruption cases,  $L_{\rm es}$  exceeds  $L_{\rm ac}$  when mass accretion rate is lower than  $M_{\rm E}/10^9{\rm yr}$ . The cooling effect by the surface layer disruption depends on the planetary (satellite) mass, especially in the case of Rayleigh-Taylor instability ( $L_{\rm es}/L_{\rm ac} \propto M^{-2/3}$ ). The cooling effect would be larger on such a small body as icy satellites or moon. Using the above  $L_{\rm es}$ , we find the cooling time of the 1000km-depth magma ocean from liquidus to solidus is about  $10^7 {\rm [yr]}$ , which is much shorter than conductive cooling time. But probable effect of melt extraction [Davies, 1990; Abe, 1991] would shorten the cooling time. We will apply and combine the above "accretional cooling" with other processes of heat and material transports.

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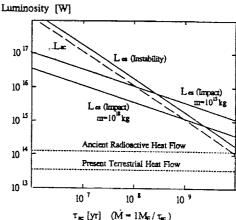


Figure 1 Disruption of the surface layer surrounding the magma ocean. (a) Infall of a planetesimal. (b) Impact disruption of the surface layer. (c) Accumulation of heavy materials. (d) Disruption of the layer by Rayleigh-Taylor instability.

Figure 2 Dependence of the heating flux  $L_{\rm ac}$  (dotted lines) and the cooling flux  $L_{\rm es}$  (solid lines) on accretion rate. Radiogenic heating data are shown for comparison.

EARLY PLANETARY DIFFERENTIATION: GEOPHYSICAL CONSEQUENCES; G. Schubert, Department of Earth and Space Sciences and the Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90024.

Differentiation of a planet can have profound consequences for its structure and thermal evolution, including core formation and crustal growth. Recent theories for the origin and evolution of the terrestrial planets and the Moon have all these bodies forming hot and cooling thereafter [e.g., (1)]. Early core formation, and in the cases of the Earth and Moon, a deep magma ocean possibly encompassing the entire mantle (2-5) are characteristic features of these models.

Secular cooling of Mars from a hot origin and cooling of the Moon from a hot initial state with a deep magma ocean have been criticized on the basis of their tectonic implications (6-8). In the case of Mars, it was thought that extension and global expansion dominated the thermal history, inconsistent with secular cooling and global contraction. It is now believed that extensional tectonic features on Mars are largely associated with the regional deformation of Tharsis while wrinkle ridges, prominent in ancient terrain, represent the global compressional deformation associated with secular cooling and contraction (1). In the case of the Moon, it was argued that the lack of compressional tectonism comparable to Mercury's lobate scarps in scale and distribution limited the contraction of the Moon to less than about a kilometer since 3.8 Gyr ago, a condition that would be violated by the purely thermal contraction of Moon models with molten or nearly molten initial states (6,8). However, Kirk and Stevenson (9) have pointed out that expansion associated with basaltic differentiation can offset the contraction accompanying planetary cooling. They presented Moon models with initial states consisting of magma oceans as deep as 400-500 km and subsolidus warm silicate cores that evolve without violating the tectonic constraint. Expansion due to heating and differentiation of the interior silicate core during the first 2 Gyr of thermal evolution offsets the contraction due to the early cooling of the solidified magma ocean and the later cooling of the silicate core. Though account of differentiation allows for Moon models with initially partially molten states, the tectonic constraint remains a difficulty for scenarios of lunar origin involving nearly total melting. The time scale for freezing of a magma ocean is so short (10, 11) that planetary expansion/contraction associated directly with the evolution of the magma ocean would not produce tectonic features able to survive the period of early heavy bombardment. Tectonic features presently observable on the terrestrial planets instead reflect contraction due to a long term cooling and expansion due to long term differentiation of basaltic crust (1, 12).

In addition to its tectonic consequences, differentiation can influence planetary evolution by redistributing the mantle radiogenic heat sources. By concentrating the radioactive elements into the melt, the mantle can be depleted of its internal heat sources upon upward melt migration and crustal formation. Differentiation of a deep magma ocean by crystal fractionation can have serious long term consequences for planetary evolution if the result is to compositionally layer the mantle. Subsolidus convection later in the evolution of the mantle could be forced to occur in layers by the compositional density differences imposed at the time of magma ocean crystallization and fractionation. Tonks and Melosh (10) have studied how turbulent convection in a

crystallizing magma ocean acts to suspend crystals and prevent fractionation; they conclude that fractional crystallization could occur in a solidifying lunar magma ocean but not in a deep terrestrial magma ocean.

The lunar center of mass - center of figure offset could reflect the asymmetric distribution of the crust (thicker on the farside than it is on the nearside (13)) or the asymmetric distribution of density anomalies in the mantle (14). The crustal asymmetry could have occurred as thermal convection in a crystallizing magma ocean swept crustal material preferentially into one hemisphere (15). Similarly, mantle density anomalies could have been preferentially located in one hemisphere through convective circulation in a magma ocean.

The Jovian satellite Io may be the only terrestrial-like body in the solar system to presently have a substantially partially molten asthenosphere or subsurface magma ocean (16). Tidal dissipation in this layer is largely responsible for maintenance of Io's volcanic activity.

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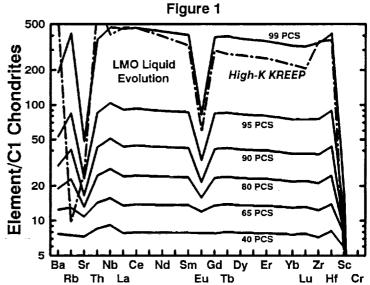
# IMPERFECT FRACTIONAL CRYSTALLIZATION OF THE LUNAR MAGMA OCEAN AND FORMATION OF THE LUNAR MANTLE: A "REALISTIC" CHEMICAL

APPROACH Gregory A. SNYDER and Lawrence A. TAYLOR, Dept. of Geological Sciences, University of Tennessee, Knoxville, TN 37996-1410.

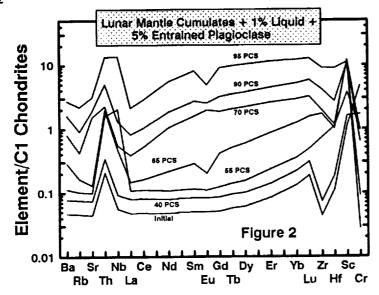
It is generally considered that lunar mare basalts were generated by the melting of a cumulate mantle formed in an early Moon-wide magma ocean or magmasphere. However, the nature and chemistry of this cumulate mantle and the logistics of its origin have remained elusive. Extensive studies of terrestrial layered mafic intrusions over the past sixty years have emphasized the imperfection of fractional crystallization and attendant crystall-crystal and crystal-liquid separation in a convecting magma chamber. These separations were similarly inefficient during evolution of the lunar magmasphere, allowing for the trapping of interstitial melt and entrainment of a small proportion of less-dense plagioclase into the more-dense mafic cumulate mush. Indeed, petrography of lunar highlands samples demonstrates this well for anorthosites (with 1-10% olivine). Therefore, we propose a "realistic" model for the evolution of the lunar mantle, which takes these observations into consideration, by the imperfect fractional crystallization of an early lunar magma ocean.

There is no doubt that a completely liquid magma ocean would have exhibited turbulent convection  $(Ra\#=10^{23}-10^{25} \text{ for a magma ocean } 400 \text{ km deep in } 1/6g, \text{ and parameters similar to those in Worster et al.,}$ [1]). However, once crystallization commences, the picture is muddled. Modelling of semi-crystalline systems is fraught with scaling and perceptual problems (witness a recent heated debate on this issue, [2],[3]). Recently, Spera [4] has come out in support of earlier work [5] which suggested that subsolidus convective overturn of the mafic cumulate mantle would be possible. However, models of magma ocean-wide convective overturn of the mantle are set-up to be self-fulfilling. Initial conditions are too simple and physically not realistic. Both Spera [4] and Herbert [5] assume that the magma ocean was completely crystalline before the first overturn in the cumulate pile. Convective overturn of the cumulate mantle may indeed occur, but may not happen on an ocean-wide scale and is more likely to occur at some critical point where the density contrast in the overlying cumulate is just in excess of that needed to initiate bouyancy-driven overturn. Therefore, overturning would occur at various levels while the cumulate was still precipitating and the ocean was still partially liquid. Herbert [5] has stated that convective overturn was possible and likely in the cumulate prior to complete solidification (approximately 100-200 Ma) of the total magma ocean. However, for the sake of simplicity, he refrained from modelling overturn in an incompletedly solidified lunar mantle. Physical models of the evolution of the lunar mantle should take this early overturning into account. In the ensuing discussion we will assume that, if convective overturn did operate, it was localized and did not greatly affect the integrity of separate cumulate "packets".

The proposed chemical model assumes a starting composition similar to "Standard Initial" Warren of (Mg#=0.80, $Al_2O_3 = 7wt.\%$ TiO<sub>2</sub>=0.4wt.%; [6]). No initial magma ocean depth is specified. The model includes fractional crystallization of the magma ocean (at a pressure of less than 1 kbar) and sinking of the mafic portion of the cumulate accompanied by trapping of 1% instantaneous residual liquid and entrainment of 2-5 modal% plagioclase [once it becomes a liquidus phase at 57 Per Cent Solid (PCS)]. Most of the crystallizing plagioclase floats to form the lunar highlands. Trace element evolution of the residual liquid and the maficcumulate, trapped-liquid, and entrained-



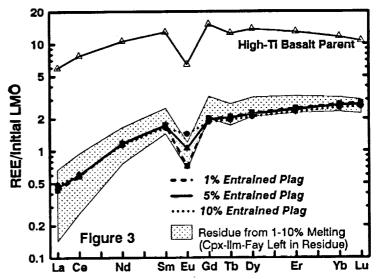
plagioclase pile is illustrated in Figures 1 and 2, respectively, and labelled with the respective PCS values. It is evident in Figure 1 that late-stage, magma-ocean, residual liquids are similar to lunar high-K KREEP [6].



In a case study utilizing our chemical model for lunar magma ocean/mantle evolution, we have modelled the melting of a source region for the high-Ti mare basalts. Many characteristics of these relatively evolved mare basalts (Mg#= 0.43-0.48,  $TiO_2=10-11wt.\%$ ) point to their generation from a late-stage Trace-element cumulate source. constraints indicate the need for a source rich in a mineral which has relatively high kps for the REE -- e.g., clinopyroxene. Other critical components in the source are fayalite and ilmenite, but also 1-3% trapped instantaneous residual liquid and 2-5% entrained plagioclase. Witness the similarity of this model source with an actual calculated residue in equilibrium

with a high-Ti basalt parent composition (Figure 3).

Major element constraints point to the need for a significant Al<sub>2</sub>O<sub>3</sub>-rich component in the source which is supplied by the entrained plagioclase in the cumulate. However, only through a process of non-modal melting, where trapped liquid, plagioclase, and ilmenite make up a disproportionate fraction of the melt, can the major element composition of the high-Ti basalt parent We differ from previous be matched. workers in not requiring a complex mixing KREEP, process involving (forsterite-rich) deep cumulates, and late (ilmenite-rich) shallow cumulates. Therefore, convective overturn of the



cumulate pile is not required on chemical grounds. Whether it is required on physical grounds is still not certain. Based mostly on high pressure multisaturation experiments of high-Ti glasses (specifically from the Apollo 15 landing site [7]) [8], it has been postulated that the high-Ti basalt source was generated at 20-25 kbar pressure (or 400-500 km in the Moon). But, the direct connection of these glasses with the high-Ti mare basalts from the Apollo 11 and 17 landing sites remains to be demonstrated [9]. Indeed, the logistics of such a deep source, which could provide unadulterated melt to the surface of the Moon, is difficult, if not impossible to rationalize.

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EVOLUTION OF A TERRESTRIAL MAGMA OCEAN: THERMODYNAMICS, KINETICS, RHEOLOGY, CONVECTION, DIFFERENTIATION; V. S. Solomatov, and D. J. Stevenson (Division of Geological and Planetary Sciences, 170-25, California Institute of Technology, Pasadena, CA 91125, U.S.A.)

Evolution of an initially totally molten magma ocean (1-4) is constrained on the basis of analysis of various physical problems in the magma ocean. First of all an equilibrium thermodynamics of the magma ocean is developed in the melting temperature range. Three components (olivine and two pyroxines or their high-pressure modifications - for the upper mantle; Mg-enriched perovskite, wüstite, periclase - for the lower mantle) are supposed to form an ideal system with one solid solution (between pyroxines and between wüstite and periclase). The chemical potentials both for the liquid and solid solutions are taken as for ideal solutions and the thermodynamical parameters are found with the help of the Gibbs free energy. Despite the simplicity of the model the comparison with experimental data at small pressures is sufficiently good. For the upper mantle the model is fitted with the help of all available data for chondrites and peridotites. For the lower mantle only different data on the melting curves are used. At pressures  $0-15\ GPa$ the crystallization sequence in this model is olivine-pyroxene solution, at 15-23 GPa - pyroxene solution-olivine, at 23-136 GPa - perovskite- magnesiowüstite or in some cases the last sequence is reversed to magnesiowüstite-perovskite despite the less concentration of magnesiowüstite. The equilibrium thermodynamical parameters are found as functions only of T and P and are used in the subsequent models of kinetics and convection.

Kinetic processes determine the crystal sizes and also determine a non-equilibrium thermodynamics of the system. When the temperature of a moving element of fluid drops below the liquidus or below subsequent phase boundaries the crystals of the correspondent solid phase nucleate and grow. Analytical solutions for different mechanisms of crystal growth are found. Results are in good agreement with laboratory and numerical experiments on nucleation and crystal growth at constant heat flux from the system and at constant temperature drop rate (5) (these experiments turn out to be very close to the problems considered). The size of the crystals depends mainly on the convective velocities, on the adiabatic gradients before and after phase boundary and on a kinetic parameter which is of the order of the peak rate of the crystal growth. Influence of other parameters is logarithmically weak. Some kinds of Ostwald ripening take place in the final stage of the crystal growth and after exit from the field of stability of the considered phase the crystals of this phase dissolve. Ripening processes are mostly important in the case of the solidification of the upper parts of the mantle (when the field of stability of phases can occupy the total convective region). The crystal size for different minerals is estimated with the help of an extrapolation of the available experimental data or theoretically. The most probable size range is  $10^{-2} - 1 cm$ .

Rheology controls all dynamical regimes of the magma ocean. The models of the steady-state rheology of partially molten systems are developed on the basis of consideration of interparticle forces due to two kinetic processes – polymerization and sintering – with the help of a general approach based on the calculation of dissipation in the shear flow. For a given composition the rheology can be Newtonian, power-law or with an apparent yield stress in dependence on the crystal fraction (or the temperature) and strain rate (6). Two sharp rheological transitions are possible: when the crystal fraction exceed the percolation threshold for the formation of the crystalline network (about 20 % of crystals) and when polymeric bridges between the crystals are changed by solid bridges (near the maximum crystal fraction for a suspension which depends on the crystal size distribution and for a bimodal distribution is 64-86 %).

The thermal convection models for different rheological laws are developed both for the laminar convection (see also (7)) and for the turbulent convection in the case of the equilibrium thermodynamics of multiphase system. Effects of rotation and non-equilibrium thermodynamics are estimated. A specific kind of compositional convection in the magma ocean occurs in addition to the thermal convection. It is due to a nonuniform differentiation of the initially stable system (essentially the same phenomenon was described in (8)). This causes a gravitationally unstable stratification. Rayleigh-Taylor instabilities and the compositional convection result in an effective remixing even in the almost solidified magma ocean. The criteria for suspension of crystals in a laminar or turbulent convective magma ocean are found. Two requirements are used: that the integral work done by convection per unit time must be larger than that of the gravitational forces acting on the crystals and that the forces due to the pressure fluctuations must be larger than the gravitational forces acting on the crystals. The last requirement is stronger because it takes into account local conditions (e. g. near the boundaries). Both criteria are qualitatively similar and include not only the ratio of the terminal velocity of the crystals to the convective velocity but also the ratio of the crystal size to the thickness of the convective layer, the crystal fraction and the convective Reynolds number. This theory explains the experimental results (9).

The evolution is estimated on the basis of all the above analysis. Most models predict that the first and subsequent solid phases begin to appear at the bottom of the magma ocean and then these boundaries rise up. In the first approximation the following dynamical regimes can be distinguished: turbulent thermal or combined thermal and compositional convection without sedimentation, turbulent thermal and compositional convection with sedimentation, laminar thermal and compositional convection with sedimentation (or with compaction and percolation). These regimes are stratified with the depth in the above order and appear from the bottom of the magma ocean. All transitions between the dynamical regimes occur in a small vicinity of the maximum crystal fraction. The differentiation is shown to begin only when different kinds of crystals are present in the solid fraction and thus geochemical models of partioning of minor elements must suppose differentiation of not just a pure first liquidus phase (10,11,12) but of a mixture of different phases. However the fractional differentiation in the uppermost part of the mantle is still possible. Convection is able to remix the mantle before it will be completely solid. This effect is due to dramatical changes of the effective thermodynamical parameters due to the presence of the melt and also due to a relatively small viscosity (in comparison with a pure solid) of this partially molten system. Possibly the final stratification consists of an primitive crust, an iron-enriched liquid layer at the core-mantle boundary and non-uniformly remixed mantle. After this moment (after  $10^7 - 10^9$  years of the evolution) the one-phase solid-like rheology convection begins to play the major role in the subsequent evolution.

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DYNAMICS AND EVOLUTION OF A MAGMA OCEAN; D. J. Stevenson, Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125.

The prevailing view (1) of very large impacts during earth accretion suggests an "initial" state for earth evolution that was totally molten or nearly so. The problem we confront is to understand the evolution from this state to an almost completely solidified mantle. Is the resulting endstate of magma ocean freezing compatible with the geological record, inferred mantle structure and evidence from geochemistry? Does the freezing event leave a signature that we can discern in the present earth?

It is first useful to set the scales for various basic phenomena. A post-giant impact earth may radiate with an effective temperative of around 2000K. For the resulting black body radiative loss, the earth can cool by a few thousand degrees (from highly superliquidus to the liquidus) in of order 10<sup>3</sup> years. For the corresponding heatflow, Kolmogarov scaling predicts corrective velocities of order 10<sup>2</sup>cm/s. A crystal substantially less or more dense than this liquid will be advected by these flows with little relative settling if it is of order 1 cm or less in size. The more difficult questions concern the growth of crystals and the rheology of the two phase medium (the liquid-crystal mush). These are dealt with in far more detail in the companion contributed paper (Solomatov and Stevenson; henceforth SS). SS find that the kinetics and Ostwald ripening of crystals limit their size to a regime in which there is little or no separation of crystals from liquid during the period of turbulent convection. Separation can only occur once the transition is made to a solid but deformable matrix with interpenetrating melt (with melt fraction of 20-30%). At this stage, the deep mantle melt is *more* dense than the coexisting solid because it is iron-rich(2). Thus, differentiation leads to a bottom layer that is iron-rich; an iron-depleted "middle" mantle and a less differentiated "upper" mantle. SS find that the middle and upper mantles can remix by a Rayleigh-Taylor instability, leading to a state that creates none of the geochemical problems emphasized by Ringwood(3). The fundamental conclusion is that there is no conflict between a completely molten initial earth and the subsequent evolution inferred from geology, geophysics and geochemistry.

The emphasis in this keynote introduction will be to set the stage for the more detailed analyses to follow and to clarify the crucial questions and uncertainties.

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## EVIDENCES FOR THE TERRESTRAL MAGMA OCEAN FROM HIGH-PRESSURE MELTING EXPERIMENTS:

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In order to study the early evolutionary history of our planet, I have carried out a series of melting experiments on primitive mantle peridotites (Takahashi & Scarfe, 1985; Takahashi, 1986; Ito & Takahashi). Using a new multi-anvil apparatus (SPI-1000) established in Tokyo Institute of Technology (T.I.T.) in 1991, I am revisiting the melting study on mantle peridotites and also started a melting study for representative chondrite compositions in the pressure range to 25 GPa. The updated phase diagram for the peridotite KLB-1 is shown in Fig. 1. Preliminary melting phase diagram for Allende C3 chondrite is shown in Fig. 2. The liquidus and solidus of the Allende chondrite are extrapolated based on experimental results by Agee (1990) at 24 to 26 GPa on the same rock.

The upper temperature bound for the terrestrial magma ocean (if it existed) should be contrained by the liquidus and solidus of the peridotite KLB-1 (Fig. 1), where the starting material is free of volatiles and highly reduced (so that high in Mg\* number). The lower temperature bound for the magma ocean may be represented by the liquidus and solidus curves of the carbonaceous chondrite (Fig.2), where appreciable amount of volatiles (H<sub>2</sub>O, S, etc.) are present and oxidized silicates are low in Mg\*. The Clapeyron-Clausius slopes for melting of both materials are small at pressures above about 10 GPa. Melting study on MgSiO<sub>3</sub> perovskite at lower mantle conditions (Heinz & Jeanloz, 1987) further confirmed the small dT/dP slopes of earth building materials at high pressures. Accordingly, small increase in mantle temperature is found to be sufficient to melt our planet to a very depth.

Based on detailed melting study on mantle peridoties (e.g. Takahashi & Kushiro, 1983), a numerical melting model for the mid-ocean ridge (MOR) system has been constructed (McKenzie & Bickle, 1988). Potential mantle temperature (PMT) of the modern Earth is estimated to be 1280°C on the basis of the MOR model. If the PMT of the Earth has cooled by ~300°C over the last 3.7 Ga as suggested by the petrogenesis of Archean komatiites (Fig.3), the existence of deep terrestrial magma ocean in the Hadean is an unavoidable conclusion.

Unique features of the Earth's Moon; 1) unusually large mass and momentum, 2) lack of large metal core, 3) early (≥4.5Ga) differentiation history, 4) akinship to the Earth in isotopes and nonvolatile trace elements, must have crucial keys to the early evolution of our planet. The single giant impact for the lunar origin must have caused a total melting and complete rehomogenization (Stevenson, 1989). If the Moon has separated from the Earth due to numerous noncatastrophic small impacts (Ringwood, 1991), the Earth then must have covered by a thick magma ocean due to the large gravitational energy liberated by rapid core formation.

Figs.1 and 2: Melting phase relations of peridotite KLB-1 and Allende C3 chondrite.

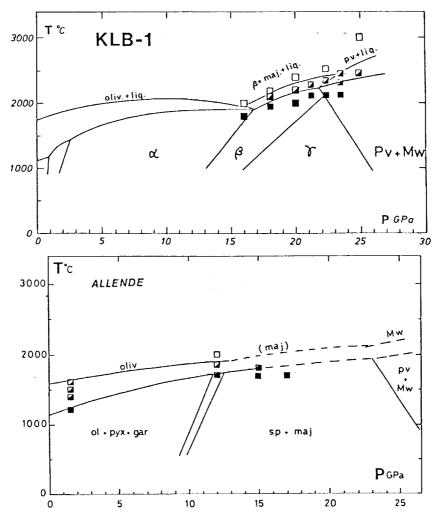
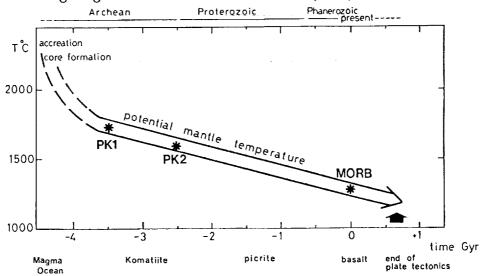


Fig. 3: Estimated secular variation of the PMT (potential mantle temperature) of the earth based on magma genesis model. After Takahashi (1990).



EVIDENCE FOR MAGMA OCEANS ON ASTEROIDS, THE MOON, AND EARTH G. Jeffrey Taylor and Marc D. Norman, Planetary Geosciences, Dept. of Geology and Geophysics, SOEST, Univ. of Hawaii, 2525 Correa Rd., Honolulu, HI 96822

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### INTRODUCTION

There are sound theoretical reasons to suspect that the terrestrial planets melted when they formed. For Earth, the reasons stem largely from the hypothesis that the Moon formed as a result of the impact of a Mars-sized planetesimal with the still-accreting Earth. Such a monumental event would have led to widespread heating of the Earth and the materials from which the Moon was made [1-3]. In addition, formation of a dense atmosphere on the Earth (and possibly on the Moon) would have led to retention of accretional heat and, thus, widespread melting [4-7]. In other words, contemporary theory suggests that the primitive Moon and terrestrial planets had magma oceans.

If magma oceans existed, they should have left geochemical and petrologic fingerprints. This paper reviews the evidence. Our approach is to ignore the theoretical reasons for why there ought to have been magma oceans and, instead, to search for chemical signatures. This approach is useful in two ways: First, and most important, if evidence for magma ocean fractionation is lacking, as some authors argue for Earth, then the processes that operated in it or after its solidification did not leave obvious geochemical clues. This, in turn, could lead to an improved understanding of the processes operating inside huge magma systems or improved knowledge of early planetary evolution. Second, one ought to leave open the possibility that the planets were not heated extensively enough to form magma oceans; for example, perhaps our present view that accretion leads almost inevitably to giant impacts has overlooked some hitherto unknown factor.

What is a magma ocean? This is an important question because planets might partially melt substantially, but not produce a large (100s of km) layer of molten fluid, leading to different products than from a much greater degree of melting. We propose that a useful definition involves two factors: (1) The magma behaves rheologically as a liquid, hence has < 50% suspended crystals [e.g.,8]; and (2) the magma encompasses a substantial fraction of the body, say > 10% (equivalent to about 170 km deep on the Moon and about 600 km deep on Earth).

What products does one expect from a magma ocean? All geochemical tests described below predict certain products (plagioclase-rich crust on the Moon, nonchondritic Ni/Co or Sm/Hf in Earth's mantle). This is a tricky business. First, there are great uncertainties in the starting compositions. Do we really know the composition of Earth's "primitive mantle"? Can we really use mantle nodules to infer what the mantle was like 4.5 Gy ago? Wouldn't dynamic convection, magmatism, and recycling since then have changed the nature of the mantle? Do we know the composition of the magma ocean? How well do we know the composition of bulk Moon? Second, what chondrite group do we use for comparison? For example, the Mg/Si ratio plays an important role in testing whether the Earth had a magma ocean, yet this ratio varies from about 0.7 in E chondrites to 1.0 in C3V chondrites. Third, in spite of great progress during the past two decades in understanding what happens inside large magma bodies, there are undoubtedly important details of many processes that may have operated that we do not understand. Furthermore, there might be crucial nonlinear relationships between processes that give rise to unexpected products. It is naive to think that the products of extremely complicated processes will be simple and easily predicted. This is not to suggest that the task is hopeless (if it were, we would not complete this review!), but only to point out that there are great uncertainties in our knowledge of bodies and processes. Of course, it's actually a blessing: everyone has lots of room to maneuver.

## METEORITE EVIDENCE FOR ASTEROID MELTING

Several types of igneous meteorites provide evidence that asteroids melted enough to form magma oceans.

Magmatic iron meteorites almost certainly formed by fractional crystallization of metallic magmas [9]. Elemental trends (e.g., Ir vs Ni) for iron meteorite groups such as IIIAB show no evi-

dence for equilibrium crystallization or the presence in the magmas of residual, unmelted crystals. Thus, the metallic magmas were at their liquidi. The IIIAB parent magma contained only 20 mg/g of S [10,11], which corresponds to a liquidus temperature of 1743 K [12]. In turn, this corresponds to 75 to 90% melting of the associated silicates. Melting of an asteroid with the composition of an H-chondrite requires a lower temperature, about 1700 K, corresponding to 65 to 80% melting of the associated silicates. It appears that the bodies in which iron meteorites and (by extrapolation) M-asteroids formed melted sufficiently to have had magma oceans. Note that we may not have samples of the differentiated silicates from these bodies.

Pallasite meteorites consist of metallic Fe,Ni (kamacite and taenite) and olivine, and probably formed at the boundary between the core and mantle of one or more differentiated asteroids [e.g., 13,14]. Their key characteristic is that they contain only metal and olivine. This implies that their parent asteroids were heated to the point where the only silicate mineral remaining was olivine. The percentage of melting required can be estimated from phase equilibria. Using a program developed by John Longhi [15], Taylor [16] showed that equilibrium partial melting of the silicate portion of H chondrites reaches the point where only olivine is on the liquidus at 40% melting, almost enough to satisfy our criteria for a magma ocean. Furthermore, to obtain the forsterite content of the olivine in main-group pallasites (Fo<sub>90</sub>) requires 70% melting, if H-chondrites represent a reasonable estimate for the starting composition of the parent asteroid. The pallasite metal-sulfide assemblage contains variable amounts of FeS, but even the highest sulfide content measured, 6 vol% in Albin [13], represents a liquidus temperature of 1710 K, about the same as H chondrites. This corresponds to silicate melt fractions of about 70%. So, the existence of pallasites seems to require formation of a magma ocean.

Enstatite achondrites, or aubrites, are fragmental breccias dominated by iron-free enstatite. Although brecciated, many igneous-textured clasts occur in them [17,18, and our unpublished data]. These rock fragments consist mostly of enstatite, with minor forsterite and diopside. The abundance of diopside (high-Ca pyroxene) lamellae in enstatite allows us to infer that the low-Ca pyroxene crystalized as protoenstatite, orthoenstatite, and possibly pigeonite because these minerals vary in Ca content [19]. Textures such as complex reentrant forms indicate that the pyroxene grains are not cumulus; they appear to have crystallized from an ultramafic magma [18]. This requires almost complete melting of a composition like that of the average aubrite, again suggesting a magma ocean.

Formation of the unique Shallowater enstatite achondrite also involved almost complete melting of a small asteroid [20]. This meteorite consists of large enstatite crystals up to 4.5 cm long that enclose unmelted xenoliths of another enstatite-rich assemblage. Its origin involved impact-induced mixing of the xenolith assemblage into a melt of essentially pure enstatite. This unusual melt would have had a liquidus temperature of about 1850 K.

Apparently, high-temperature silicate magmas (i.e., magma oceans) were not uncommon among asteroids. This has implications for the geochemistry of the Earth because some processes, such as metal segregation, would have taken place in planetesimals at low pressures, not the high pressures prevailing inside the Earth [21,22]. If metallic cores did not reequilibrate with silicates inside the Earth, siderophile element concentrations in the mantle would be different from those expected based on high-pressure equilibration.

Not all asteroids melted, of course. Chondrite parent bodies and C, P, and D asteroids are almost certainly undifferentiated. Since some formed magma oceans and others did not melt at all, there must be many that melted substantially, but not enough to form magma oceans, as defined above. These are interesting cases to study because they hold clues to differentiation, albeit at low pressures, without a magma ocean epoch. Examples include many types of stony-iron meteorites and possibly many S-asteroids.

#### THE MOON

Warren [25] summarizes evidence for the lunar magma ocean; a concise summary is also given in Heiken et al. [26, Chap. 2]. We update the main arguments here, with special consideration to uncertainties and counter arguments.

The magma ocean concept was inspired by a few white fragments in the charcoal gray Apollo 11 soil [23,24]. The original idea was that the highlands crust is composed predominately of anorthosite. Such an enrichment in one mineral, it was argued, requires crystal fractionation: plagioclase floated in an ocean of magma. Although now complicated by an improved knowledge of the lithologic diversity of the lunar crust, this is still the best argument for the existence of the lunar magma ocean. The central question is whether there is an enrichment in plagioclase in the lunar crust. Assessing this is complicated by several factors: (1) Igneous activity has greatly changed the composition of the initial lunar crust. A wide variety of highland rock types has been recognized [26, Chap. 6]. This magmatic activity diluted any initially high concentration of plagioclase and transferred much of the Moon's inventory of REE and other incompatible elements into the crust. (2) Our sampling is limited to six Apollo and three Luna sites, supplemented by several lunar meteorites from unknown highland areas. Remote sensing data suggests that our sample collection is not representative. (3) We do not have global geochemical and spectral coverage of the Moon.

The Moon's crust is certainly enriched in plagioclase relative to the bulk lunar composition or the mantle. How much plagioclase ought the crust above a magma ocean have contained? There is no reason to expect it to be 100% plagioclase. Although many lunar ferroan anorthosites (the candidates for magma-ocean cumulates) are > 98% plagioclase, many clearly related rocks contain substantially more mafic silicates, up to 30% (36 wt%) [27]; the mean of large samples is 8.1 + 1.0 + 1

What is the crust like? Most estimates converge on the upper crust averaging 26-28 wt% Al<sub>2</sub>O<sub>3</sub> [25,27,28]. These estimates are based on lunar sample analysis, orbital geochemistry, geophysical considerations, and analysis of lunar meteorites. Furthermore, the crust is not uniform; some areas seem to consist of 70-85 wt% ferroan anorthosite [29] (this assumes ferroan anorthosites are almost pure plagioclase). Detailed mass-balance calculations by Korotev and Haskin [30] confirm the abundance of ferroan anorthositic rocks: they calculate that the crust consists of 73% ferroan anorthositic rocks and only 27% other types of highland rocks. Their ferroan anorthosite component was modeled as two separate components, one like rock 15415 (99.5% plagioclase) and one like rock 67215 (85% plagioclase). Thus, it appears that the crust is enriched in rocks of the ferroan anorthosite suite, the proposed magma ocean product. This product was not simple, however. Not only did the abundances of mafic minerals and plagioclase vary, but the ferroan anorthosite suite can be divided into at least four subgroups [31]. Furthermore, some individual ferroan anorthosites have had extremely complicated histories [32]. This is consistent with the complexity expected in a huge magmatic system such as the magma ocean.

The second most useful line of evidence is the complementary Eu anomalies in ferroan anorthosites (positive) and mare basalts (negative). The latter inherited their anomalies from their mantle source regions, not by plagioclase fractionation (though there are ways around this, discussed below). The idea is simple: plagioclase crystallization depleted the magma ocean in Eu. Mafic minerals crystallizing from the depleted magma would then have negative Eu anomalies. Subsequent remelting of the mafic cumulates yield mare basalts with negative Eu anomalies. Simple and elegant. Also oversimplified. As Ryder [33] summarizes, the connection between mare basalts and ferroan anorthosites is not quite so direct. For example, the mare basalt source regions are too magnesian to have crystallized from the magma that gave rise to even the most magnesian ferroan anorthosites. Assuming that the Moon does not contain unsampled magnesian anorthosites related to the ferroan anorthosite suite, the logical conclusion is that ferroan anorthosites formed after at least some of the mare source regions crystallized. That alone is not inconsistent with the magma ocean concept because an ultramafic melt will crystallize olivine and pyroxene before becoming saturated with plagioclase. However, it does not explain how the mare basalt source regions acquired their Eu anomaly. Ryder [33] reconciles this and other inconsistencies by proposing that the Moon experienced a period of massive overturning after the magma ocean had crystallized. In spite of the inconsistencies, the basic fact remains: ferroan anorthosites, which make up >70% of the crust, have large positive Eu anomalies. Where, if not mare basalt source regions, are the complementary mafic cumulates depleted in Eu?

Alternative explanations for producing the negative Eu anomalies in mare basalts have been proposed [34-36], some evoking complex magma chamber processes and others requiring specific source mineralogy. All these models suffer more difficulty than the magma ocean model. Magma chamber models require repeated replenishment of mare basalt magma chambers and that all mare basalt samples, including unfractionated, magnesian pyroclastic glasses, went through such a stage in their evolution. This seems unlikely. The idea that negative Eu anomalies in some types of mare basalts could have been produced without prior plagioclase crystallization [35,36] has been shown to be inconsistent with the REE patterns of mare basalts [37].

Finally, Kirk and Stevenson [38] have taken a new look at the stress history of the Moon. Although not absent, compressional and tensional features are rare on the Moon. This means that the Moon's radius could not have changed by more than 1 km since 3.8 Ga. There has been debate about the implications of this for the extent of early lunar melting [e.g., 39,40]. Kirk and Stevenson take a new approach in calculating volume change during cooling. They conclude that the observed paucity of tectonic features is consistent with the Moon being initially 50% molten.

### THE EARTH

Several investigators have searched for evidence that the Earth had a magma ocean. Results are contradictory. The most important reason why interpretations differ stems from differences in the choice of partition coefficients (major, minor, and trace elements) used for the high-pressure minerals thought to have been involved in a fractionating terrestrial magma ocean: olivine, perovskite, and majorite garnet. Differences in interpretation also arise from judgments as to what serves as a compositional base for comparison. Some authors test fractionation models against CI-normalized compositions [41-43]. For example, Sc/Sm, Sm/Hf, and Hf/Lu ratios are useful for testing perovskite fractionation. However, other chondrite groups are equally valid possibilities for the primitive Earth, and these differ substantially from CI in these elemental ratios, making it difficult to test for perovskite fractionation [44]. Others authors [45-47] emphasize the importance of comparing fractionation models to the composition of the upper mantle as deduced from carefully-selected mantle nodules [48].

Ohtani [49] suggested that perovskite fractionation was involved in the evolution of the Earth's mantle. Agee and Walker [50] studied this concept in detail for major elements and concluded that perovskite could have fractionated by sinking in a terrestrial magma ocean while olivine floated to the point at which it became neutrally buoyant (about 250 km depth). This accumulated olivine (30%) then mixed by solid-state convection into the upper mantle, accounting for the high Mg/Si ratio in the upper mantle. McFarlane and Drake [46] pointed out that accumulation of olivine into the upper mantle would also affect other elemental ratios, such as Ni/Co. This ratio is at present chondritic in the mantle, so if olivine accumulation occurred the ratio of the Ni and Co partition coefficients must not be drastically different from 1. Results of calculations suggest that olivine accumulation would, indeed, drive Ni/Co away from chondritic, arguing against substantial olivine accumulation.

The suggestion of perovskite fractionation has also been tested [50, 41-43]. Ringwood and coworkers [41-43] use their data for distribution coefficients to argue that Sm/Hf, Sc/Sm, and Hf/Lu are chondritic in the upper mantle, so perovskite fractionation could not have taken place. However, Walker and Agee [44] counter that perovskite fractionation is allowed if one uses partitioning data obtained by Ito and Takahashi [51], and point out in detail the difficulties of high-pressure experiments. There is clearly a need for continued experiments at high pressures and for an assessment of which data are the most realistic and how to obtain better data.

Garnet is a logical choice for a fractionating mineral. Hertzberg [52,53] argues that evolution of the mantle involved fractionation of majorite garnet, a form of garnet that approaches pyroxene in composition and exhibits extensive solid solution. Agee and Walker [44] argue that majorite liquidus compositions rule it out a an important fractionating phase in a magma ocean. Other studies [41-43,45,47] use trace element data to argue against majorite fractionation. In this case, four sets of experiments from three groups yield consistent values for partition coefficients, so the conclusion seems firm. However, Hertzberg and Gasparik [53] argue from experiments and thermodynamic reasoning that the pressure effects on the compositions of liquidus garnets and majorites are very strong and must

be taken into account. Their calculations using their values for distribution coefficients suggest that the primitive mantle could have formed by 35% fractionation of majorite garnet, if the starting composition was like CV chondrites. They do not consider trace element fractionation, however.

Rama Murthy [54] has approached the problem from a different perspective. He focuses on siderophile element abundances in the mantle, which are greater than one would expect from metal-silicate equilibrium. The apparent enrichment in siderophile elements has led to ideas [55] such as inefficient core formation and accretion of a late veneer. Rama Murthy points out that the metal-silicate equilibrium would have taken place at very high temperatures if the Earth formed as hot as generally thought [1-7]. This leads to recalculation of distribution coefficients measured at 1573 K to higher temperatures, using simple thermodynamic arguments, assuming ideality, and ignoring pressure. The result is a reasonable match between predicted and observed siderophile abundances in the mantle. If verified, the high temperature required supports the concept that the Earth had a magma ocean. However, note that Rama Murthy's suggestion of the importance of high-temperature equilibrium does not apply to fractional crystallization of olivine, perovskite, or other phases because they form at the liquidus, not > 3000 K.

In summary, the balance of evidence suggests that fractionation of majorite garnet played at best a minor role in fractionation of a terrestrial magma ocean. Evidence for fractionation of olivine and perovskite is ambiguous. Resolution of the problem requires additional experiments at high pressures. The suggestion that equilibrium between metal and silicate melt took place at very high temperature, which leads to changes in the partition coefficients, supports the magma ocean concept but needs experimental verification.

As pointed out by McFarlane and Drake [45-47], if it turns out that crisp evidence for a terrestrial magma ocean is lacking, then there are profound implications. First, of course, the Earth might not have had a magma ocean. If not, then the Moon might not have formed by a giant impact, as such an event would surely heat the Earth substantially. Alternatively, the magma ocean expected to have formed might have never produced a stratified product because of the nature of the processes operating in the large terrestrial magma system [56]. A third alternative is that an originally-stratified mantle was homogenized by vigorous solid-state convection after the magma ocean solidified. If rehomogenization occurred, however, it must have taken place rapidly: zircons from Western Australia are 4.2 Ga and have primitive Hf isotopic ratios [57]; thus, they crystallized in a system with chondritic Hf/Lu. In other words, if magma ocean crystallization produced a stratified mantle, it had to rehomogenize by 4.2 Ga. No matter which of these is correct, if the Earth did melt, it formed with a high Mg/Si ratio, different from most chondrites. This implies that the Earth accreted materials from its vicinity at 1 A.U. and was not mixed with planetesimals from the asteroid belt (2-4 A.U.), the source of chondrites.

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66 MAGMA OCEAN FORMATION DUE TO GIANT IMPACTS; W. B. Tonks and H. J. Melosh. Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721;

Introduction: The effect of giant impacts on the initial chemical and thermal states of the terrestrial planets is just now being explored. Several authors (eg. Melosh, 1990; Benz and Cameron, 1990; Stevenson, 1987) have noted that the putative Moon-forming giant impact has tremendous thermal effects on the Earth, including extensive vaporization and melting. These authors suggest that one result of such an impact is the creation of a magma ocean. Because impacts between the proto-Earth and bodies the mass of Mercury or larger occur more than once during late stage accretion (Wetherill, 1988), it may be possible for multiple magma oceans to form. Magma ocean formation by impacts depends on the volume of melt produced in the collision and the planet's ability to rapidly regain hydrostatic equilibrium. To our knowledge, estimates of these factors have not been made. We constructed a model that estimates the volume of impact melt produced in a large collision to examine the ability of large impacts to trigger core formation (Tonks and Melosh, 1991). We now use our model to estimate the melt volume produced in a giant impact and examine the effect of gravity on the geometry and evolution of the melt region.

Modeling. A large, high speed impact creates an approximately hemispherical melt region with a radius that depends on the projectile's radius and impact speed. The excavation flow, however, is much shallower than hemispherical. In small impacts, the melt region is almost entirely contained within the volume excavated from the crater. However, as the radius and impact speed of the projectile increase, a larger fraction of the melt is produced below the excavation zone and hence is not excavated. We call this fraction the "retained fraction". The larger the planet's gravity, the less material is excavated by a projectile with the same mass and impact speed. In the largest impacts on large planets, craters may form entirely within the melt region. The retained fraction is important in determining the melt available for formation of a magma ocean because melt excavated from the crater cools quickly and probably does not contribute to the ocean. A very

large impact can create a deep, intact melt region that might form a global magma ocean.

Numerical calculations (eg. O'Keefe and Ahrens, 1975) show that the shock pressure has two distinct dependences on distance from the impact site. Near the impact site, shock pressure declines slowly. This region is designated as the "isobaric core" and within it we assume the pressure is constant. The shock pressure is given by the second Hugoniot equation:

$$P-P_0 = \rho u_p U \tag{1}$$

where P and  $P_0$  are the shock and ambient pressures,  $\rho$  is the material's density,  $u_p$  is the particle velocity, and U is the shock velocity. Outside the isobaric core, pressure declines rapidly with distance. Most materials exhibit a linear relationship between the particle and shock velocity:

$$U = C + Su_p \tag{2}$$

where C and S are measured parameters of the material. Outside the isobaric core, the particle velocity decreases with distance by a power law relationship (Perret and Bass, 1975):

$$u_{D}(r) = u_{DO}(r_{O}/r)^{-n}$$
 (3)

where  $u_{po}$  and  $r_{o}$  are the particle velocity and radius of the isobaric core. The power n was measured as 1.87 in alluvium by these authors. We used n = 2, the conservation of momentum value to be conservative. We used conservation of energy estimate the radius of the isobaric core.

The effects of the passing shock depend on decompression of the material from the shock to the ambient pressure. If this pressure difference is above some minimum, the material melts upon decompression. If this pressure difference is above some higher minimum, the material vaporizes. The pressure difference at which silicates melt depends on the material, but is around 100 GPa. We assumed that if the shock pressure was greater than 110 GPa, the value required for ANEOS dunite, melting occurred. We combined equations (1), (2), and (3) to solve for the radius of the melt hemisphere, assuming normal incidence. From this radius, we calculate the melt volume.

$$V_{\text{melt}} = V_{\text{proj}}(v_i/v_i^{\text{min}})^{3/2}$$
 (4)

where  $V_{proj}$  is the projectile volume,  $v_i$  is the impact speed, and  $v_i^{min}$  is the minimum impact speed required to cause melting to the edge of the isobaric core (about 7 km/sec). We calculated the retained fraction by using the excavation profile predicted by Maxwell's Z model with Z=3

(Maxwell, 1977). The retained fraction is a function of the planet's gravity, the projectile's radius, and to a lesser extent, the impact velocity. These dependencies can be estimated using the pi scaling theory (Holsapple and Schmidt, 1982):

 $f_{\text{retained}} \sim (ga)^{\beta} v_i^{(0.5-2\beta)}$  (5)

where g is the acceleration of gravity, a is the projectile radius, and  $\beta$  is the power relating  $\pi_2$  and  $\pi_D$  in pi scaling theory. It has a numerical value of about 0.22. Thus, the retained fraction increases with impact speed although the dependence is weak.

Results: Table 1 presents example results from our calculations. It lists the retained melt fraction, the melt volume created (normalized to the projectile's volume), and the depth of a uniform global magma ocean that would be formed if the retained melt were rapidly extruded to the surface. We set the ratio of the projectile's mass to the planet's mass to 0.1 and calculated the results at two impact speeds. When a Mars-sized projectile strikes the Earth, the retained melt fraction is large because the melt region extends well beyond the crater excavation zone. A global magma ocean of uniform and significant depth could be created from this melt. Asteroid-sized bodies do not form large melt regions because the lower gravity allows easier excavation.

Because the bulk density of the melt region is lower than the bulk density of the remaining solid planet, the solid will deform to return the planet to hydrostatic equilibrium, pushing the magma to the surface. If this process is rapid compared to the magma cooling time scale, a uniform depth magma ocean will form. Calculation of these time scales is extremely model dependent and depend on many poorly constrained parameters. The hydrostatic relaxation time scale depends on the effective viscosity of the remaining solid planet, which in turn depends exponentially on temperature. This time scale probably also depends on strain rate in a complex, non-Newtonian fashion. The relaxation time scale of the present Earth, measured by glacial rebound, is of the order of 10,000 years. The magma cooling time scale depends critically on the insulating properties of the atmosphere and the formation of an insulating crust. We previously calculated the time scale for cooling of a magma ocean with no insulating crust or atmosphere at about 10,000 years (Tonks and Melosh, 1990). These time scales imply that the melt region may be solidified before a global magma ocean forms. However, it is likely that a transient silicate atmosphere blankets the planet for some time after the impact, increasing the cooling time scale. Evaluation of these time scales require much more detailed work.

Conclusions: Giant impacts on large planets can create large, intact melt regions containing melt volumes up to a few times the volume of the projectile. These large melt regions are not created on asteroid sized bodies. If extruded to the surface, these regions contain enough melt to create a magma ocean of considerable depth, depending on the impact speed (mostly a function of the melt volume relationship, eq. 4), projectile radius, and gravity of the target planet.

Table 1: Melt Volume, Retained Fraction, and Magma Ocean Depths

Mproj = 0.1 Mplanet Impact Speed V<sub>melt</sub>/V<sub>proi</sub> Depth of Magma **Retained Fraction** Planet Mass Ocean (km) (km/sec) (kg) 6x10<sup>24</sup> (Earth) 300 0.88 1.6 10 1980 6x10<sup>24</sup> (Earth) 0.92 4.6 20 1.6 30 1x10<sup>23</sup> (~Moon) 10 0.286 92 20 0.298 4.6 1x10<sup>23</sup> (~Moon) 2 1x10<sup>22</sup> (~2xCeres) 10 0.033 1.6 1x10<sup>22</sup> (~2xCeres) 20 0.035

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### INHERITANCE OF MAGMA OCEAN DIFFERENTIATION DURING LUNAR ORIGIN BY GIANT IMPACT

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The giant impact model for the origin of the Moon has won widespread, almost consensus, support [1-3]. It seems to satisfactorily explain the high angular momentum of the Earth-Moon system, and the strong depletion of FeNi in the Moon. This model is usually assumed to entail no significant fractionation of nonvolatile lithophile elements relative to a simple binary mixture of impactor silicates plus protoearth silicates. If anything, the most refractory elements (Al, Ca, Sc, Ti, V, Y, Zr, Nb, REE, Hf, Ta, Th and U) are sometimes assumed to be enriched as a cohesive group. However, the mechanism of giant impact seems likely to derive the Moon selectively from the peripheral portions of the impactor and the Earth. Although the Earth may have been hot enough before the impact to be completely molten, analysis of the likely number and timing of major impacts in the prehistory of the impactor indicates that a fully molten, undifferentiated condition for that relatively small body is unlikely. Given selective sampling by the giant impact, any significant vertical differentiation within the noncore portion of the impactor would have been largely inherited by the Moon.

In a typical model of Melosh and Sonett [2] (their Fig. 5), the innermost 40 vol% of the noncore portion of the impactor contributes only 5 vol% to the jetted matter that eventually forms the Moon. Analogous figures for the smoothed particle hydrodynamic (SPH) models of Benz et al. [1,4] are not yet available, but in at least some of their models the Moon is derived almost entirely from a single quadrant of the impactor [1], and yet no core matter gets included. It seems unlikely such an otherwise selective sampling of the impactor would not also be depth-selective within the noncore region. The jetting model [2] is probably far more depth-selective than any variant of the SPH model. However, this contrast is effectively offset by the higher ratio of protoearth-derived vs. impactor-derived matter in the jetted matter (typically about 1:1) than in the protolunar matter of the SPH models (typically about 16:84).

Only a few impacts capable of fully melting the Mars-sized impactor could have occurred during its entire history. The mass spectrum of planetesimals is commonly assumed to follow a power law of the form  $N(m) = C m^{-q}$ , where N(m)dm is the number of planetesimals with masses between m and m + dm, and C and q are constants. It seems probable [e.g., 3] that q falls between 5/3 (the value for which each mass decade has an equal amount of cross-sectional area) and 2 (the value for which each mass decade has an equal amount of mass). Given this mass spectrum, the expected, or most likely, number of impacts large enough to engender total melting in the history of a 1.5-Mars-sized impactor body is between 2 and 8. The time before the Earth collides with a 1.5-Mars-sized body is generally expected to be of the order 5-50 Ma [3]. However, the impact that forms the Moon must occur relatively late, when the Earth is almost fully grown. Thus, the prehistory of the Moon-forming impactor probably spanned >>20 Ma, and most plausibly >40 Ma [3]. If there were 2-8 events in this prehistory that engendered total melting of the impactor, then the average interval between such events was probably of the order 1-10 Ma. A few tens of percent of the impactor's magma ocean (MO) probably would have crystallized over such an interval [5].

Based on general cosmochemical principles (and lacking any evidence to the contrary), I assume that the bulk composition of the putative impactor resembled chondritic silicates; and therefore also the Earth, which is in most respects chondritic. The precise overlap in oxygen isotopic composition between the Moon and the Earth confirms that the Moon formed out of similar parental material. If the impactor was appreciably bigger than Mars, perovskite probably crystallized along the base of its MO. Other crystals formed in the early and middle stages of MO crystallization probably included majorite and ß-spinel. Calculations indicate that even if only 10% of the impactor MO had crystallized prior to the collision, significant fractionations of ratios such as Hf/Yb, ITE/Hf, ITE/Zr, ITE/Yb, ITE/Ti, Ca/Al, and Ti/Al would have been inherited by the Moon (where ITE stands for incompatible trace elements, most notably U, Th and La). Models without perovskite engender relatively slight fractionation of Hf/Lu, ITE/Hf, ITE/Ti, etc., but lead to relatively extensive fractionation of ITE/Al and Ca/Al. A typical model, assuming 25% crystallization of the noncore portion of the impactor, in the form of 10% perovskite

followed by 15% of a 2:1 mixture of majorite + B-spinel, yields for the bulk composition of the Moon in comparison to the bulk composition of the Earth: a Ca/Al ratio enhanced by 1.28 x, an ITE/Al ratio enhanced by 1.35 x, a Yb/Hf ratio enhanced by 2.0 x, an ITE/Hf ratio enhanced by 2.7 x, etc. The bulk-Moon compositional quirk most firmly implied as a byproduct of the giant impact is enhancement of Th and U over less ideally incompatible refractory elements, such as heavy REE, Zr, Hf, and especially the major elements Al and Ca. Thus, if the giant impact model still appears plausible, heat flow should only be used to derive upper limits for most of the refractory lithophile elements.

Admitedly, these models involve great uncertainties, in the thermal state of the impactor prior to the collision, in the physical model for "sampling" the impactor as a function of depth, and in the high-pressure phase equilibria, including crystal/melt distribution coefficients, used to model MO differentiation. Most of these uncertainties could be reduced through a variety of further studies. Nonetheless, even in this preliminary form, the results indicate that the giant impact hypothesis implies a rather peculiar composition for the refractory lithophile component of the Moon. The Moon has until now generally been assumed to contain refractory lithophile elements in chondritic proportion to one another. For some ratios such as Hf/Yb [6], Sm/Al [7], and Ba/Al [8] geochemical observations appear to confirm this assumption. Unless my models grossly overestimate the magnitude of the fractionations associated with lunar origin by giant impact, the chondritic-refractory Moon hypothesis and the giant impact hypothesis cannot both be correct.

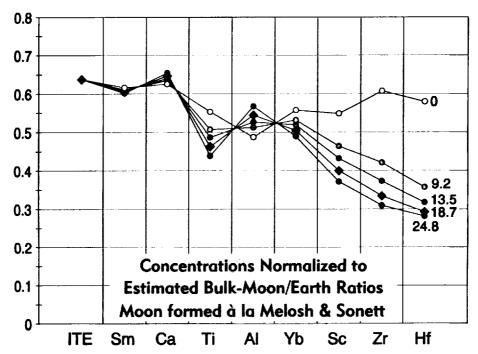


Fig. 1. Results for bulk composition of the Moon, normalized to Taylor's [9] observationally-constrained bulk-Moon composition, for models assuming lunar origin à la Melosh and Sonett [2] with 25% of the impactor MO crystallized at the time of the impact. Numbers at right ends of curves indicate the percentages of crystallization at which the crystallizing solids are assumed to change from perovskite to 2/3 majorite, 1/3 \( \textit{B}\)-spinel (these percentages are related to the mass of the putative impactor). Preliminary results for SPH-style models, extrapolated from Benz et al. [1,4], are not much different.

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#### THE THREE STAGES OF MAGMA OCEAN COOLING

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Models of magma ocean (MO) cooling and crystallization can provide important constraints on MO plausibility for a given planet, on the origin of long-term-stable (continental or "highlands") crusts, and even on the origin of the solar system. The heat-transfer and fluid-dynamical aspects of magma oceanography are usually considered to be exclusively, or almost exclusively, problems of geophysics. This view is dangerously oversimplified. Accurate modeling of the physical behavior of a MO requires complete integration of geochemical/petrological constraints on its crystallization behavior.

Available physical models typically assume that the ratio  $z/z_{mc}$  remains approximately constant (at ~0.2-0.4) throughout the first 90% or so of MO crystallization, where  $z_c$  is the thickness of the crust and  $z_{mc}$  is the thickness of the mantle cumulate zone. In other words, such models assume that the ratio of crystallization of buoyant, floating matter vs. crystallization of dense, mantle matter is a constant. By solution of the "Stefan problem," the MO crust is supposed to thicken at a rate approximately proportional to  $\gamma t^{1/2}$ , where  $\gamma$  is a constant of the order 0.01 km/yr<sup>1/2</sup>; while the mantle cumulate zone thickens at a similar but roughly 2-3 times faster rate. More realistically, however,  $z_c/z_{mc}$ , dz/dt and  $dz_{mc}/dt$  are all complex, sharply discontinuous functions of the geochemical evolution of the MO.

Assuming the MO is initially extensive enough to have a mostly molten surface, its first stage of cooling is an era of radiative heat loss from the surface, with extremely rapid convection below, and no conductive layer in between. This stage lasts until a "chill" crust develops over most of the surface. If the MO is insulated by a thick, dense atmosphere, or if the heat content of the MO is continually replenished (e.g., by continuing large impacts), the duration of this first stage of cooling is difficult to predict. Otherwise, the chill crust will develop only a few decades after the time of maximum melting.

The development of the chill crust starts the second stage of MO cooling. Heat loss is now limited by conduction through the crust. The cooling rate falls precipitously at the start of the second stage, and in general it continues to diminish as the chill crust slowly grows, at a rate proportional to  $\gamma_{cc}t^{1/2}$ , where  $\gamma_{cc}$  is an "effective" rate constant << 0.01 km/yr<sup>1/2</sup>. An "effective"  $\gamma$  is needed because the chill crust is repeatedly thinned by foundering or by being disrupted by impacts. At the same time, the MO is rapidly cooling, and  $z_{mc}$ , the thickness of the mantle cumulate zone, is growing at a rate up to several orders of magnitude faster than the rate of crustal thickening. A thick, flotation crust cannot form until a phase buoyant at low (near-surface) pressure begins to crystallize. The only candidate phase is feldspar. The MO cannot crystallize appreciable feldspar until the melt composition is sufficiently enriched in alumina to be feldspar-saturated. For reasonable overall MO compositions, 1-bar feldspar saturation requires an Al<sub>2</sub>O<sub>3</sub> concentration of at least 12 wt%, and ~15-18 wt% is probably more realistic.

The third stage of cooling starts when the near-surface MO evolves compositionally to the point of saturation with feldspar. At this point, the cooling rate again precipitously diminishes, the rate of crustal thickness growth as a function of temperature suddenly increases, and the rate of growth of the flotation crust as a function of time becomes proportional to  $\gamma_{fc}t^{1/2}$ , where  $\gamma_{fc}$  is a constant of the order 0.01 km/yr<sup>1/2</sup>, and much greater than  $\gamma_{cc}$ . During this stage, feldspar and mafic silicates form in cotectic proportions, which for a reasonable overall MO composition implies roughly equal volume proportions. Most of the feldspar floats and most of the mafic silicate sinks (or nucleates deep and remains deep). The rate of crystallization adding to the flotation crust approximately equals the rate of crystallization adding to the mantle cumulate zone. As the flotation crust grows far beyond the thickness of the chill crust, it adds stable insulation over the MO, which causes  $\gamma_{fc}$  to be much greater than the "effective"  $\gamma_{cc}$ .

The early crystallization sequence of the MO will depend on the pressures that prevail deep (at future mantle levels) within the planet. Even though heat is removed at the top of the system, the proportion of crystals growing at shallow levels will be limited, before the third stage of cooling, by the

tendency for vigorous convection to produce an adiabatic geotherm reaching very close to the surface. At least at P less than about 10 GPa, silicate-melting dT/dP is much greater than silicate-adiabatic dT/dP. Thus, within the adiabatic portion of the shallow MO, assuming the convectively stirred MO composition is roughly homogeneous, the thermal stability of any crystalline matter is directly proportional to its depth. Of course, the adiabatic regime breaks down close to the surface, within the chilled crust. Thus, crystals nucleate copiously near the MO/chilled crust interface. Until the MO arrives at feldspar saturation, most of these crystals will be mafic silicates far denser than the melt. They will sink into the MO, become swept up in the convective stirring, and eventually either remelt or become "made over" into different crystals stable near the base of the MO. A small fraction of the crystals nucleating just below the chill crust will be feldspar, produced where pockets of melt fractionate apart from the main MO (this fraction will increase as the MO composition evolves). The buoyancy of feldspar in the early, ultramafic MO will be approximately neutral. After the residual MO becomes enriched in FeO, well into the second stage of cooling, feldspar will become buoyant, and any of it not dragged down with adjacent mafic silicates will add to the bulk and buoyancy of the chill crust. But only when the MO at least nears feldspar saturation will the overall crust become more than marginally buoyant. Before feldspar saturation, the average crustal thickness will be limited by the high potential T of the MO adiabatic zone, and the crust will undergo continual foundering, as cooling increases its density, and incessant cratering causes it to be disrupted and splashed over with mafic MO melt.

The more permanent crystals grown at depth in the early MO may include a variety of phases (magnesiowüstite, perovskite, majorite "garnet,"  $\beta$ -spinel, pyroxene) stabilized by high P, in addition to (at relatively low P) olivine. A deep MO on an Earth-sized planet might crystallize all of these phases; a deep MO on a Moon-sized planet might only crystallize olivine and pyroxene. If strictly Al-poor phases crystallize from a MO that is initially of chondritic-silicate bulk composition (~3 wt%  $Al_2O_3$ ), then at least 75 wt% of the MO must crystallize before the melt composition evolves to the point (at least 12 wt%  $Al_2O_3$ ) of feldspar saturation. Some of the higher-P phases (especially majorite) that will crystallize before feldspar saturation in a MO on an Earth-sized planet will incorporate a major fraction of the inital MO  $Al_2O_3$ , and thus delay the onset of feldspar saturation. Thus, much less than 25 wt% of an initially chondritic-silicate MO will remain molten at the end of cooling stage 2 on an Earth-sized planet.

There are several important implications from this simple analysis. Barring the formation and persistence of a thick, insulating atmosphere, stages 1 and 2 will always be brief in comparison to stage 3. The solidification time for a very deep, ultramafic MO, formed by total or near-total melting of the planet, will scarcely be longer than the solidification time for a far smaller, basaltic MO, formed by a modest degree of partial melting and already saturated, or nearly saturated, with feldspar. Solomon and Longhi [1] noted that MO solidification time is "not a strong function" of initial MO depth, but even their geochemically "evolving" MO models probably overestimate the solidification times for deep MOs. The lunar MO probably took ~100 million years to reach 20 km residual thickness, regardless of whether its inital depth was 200 km or 1700 km. Also, if the MO is initially ultramafic, the effective  $\gamma$  for MO crystallization is a complex function of time, and the rate of mantle accumulation starts out much greater than the rate of crust thickening. Assuming that the Moon was formed as the result of a giant impact between the Earth and a roughly Mars-sized body, it is plausible to assume that the Mars-sized body would have had a previous history of impacts large enough to totally melt it on at least a few occasions. However, it seems unlikely that the impactor would have experienced such a collision recently enough to still be far from the end of cooling stage 2. In other words, unless it fortuitously was impacted into a fully molten state just 1-2 million years before, its mantle was probably >50% crystallized as it encountered the Earth. This raises the possibility that the differentiation within the impactor may have been partly inherited by the Moon [2]. More work on incorporating chemical constraints into "evolving" physical models of MO solidification would be highly worthwhile.

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### THE FERROAN-ANORTHOSITIC SUITE AND THE EXTENT OF PRIMORDIAL LUNAR MELTING

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The Apollo highlands rock collection includes more than 100 "pristine" fragments that survived the intense meteoritic bombardment of the ancient lunar crust with unmixed, endogenously igneous compositions. Among them there is a distinctive and numerically important (roughly 50%) group that displays highly anomalous geochemistry in comparison to all others. This "ferroan-anorthositic suite" (FAS) features remarkably low Mg/(Mg+Fe) (or mg) ratios compared to rocks that otherwise (e.g., in terms of Na/Ca) might seem geochemically similar. Another remarkable feature shared by all large FAS rocks is high feldspar content: ~77% in the mode for the least feldspathic case (60135). Aside from rocks with the distinctive FAS geochemistry, no large pristine rock has modal feldspar >77%. The averages for large pristine rocks are roughly 94% for the FAS, vs. ~51% for all other ancient cumulates [1].

The geochemical anomaly manifested by the FAS appears to reflect a geochemical, and probably also a genetic, bimodality among the ancient lunar cumulates. Early models that purported to account for this bimodality as the product of a single magma have been discredited. One still occasionally hears allusions to a superficially similar pattern among cumulates from the Stillwater complex, coupled with speculations that the FAS rocks have low mg ratios because their mafic silicates are mostly products of trapped intercumulus melt. However, even the authors who adduced the Stillwater analogy found that the FAS is too greatly unlike the other ancient lunar cumulates (collectively known as the Mg-suite) for both suites to be products of a common magma, "even under extreme circumstances" [2]. Moreover, the Stillwater complex has itself been inferred to be the product of two dissimilar intrusions of magma [3]. Also, the more mafic members of the FAS could hardly have acquired the bulk of their Mg+Fe from trapped intercumulus melt, without also acquiring enrichments in incompatible elements, the observed levels of which are in most cases low enough to rule out this model.

The FAS rocks are probably "ferroan" because they formed out of magma that had previously undergone prolonged, exclusively mafic (ol + px) fractional crystallization (FC). This process can be expected to occur in a deep, initially ultramafic magma ocean (MO), which must crystallize a huge fraction of mafic silicate before the melt Al<sub>2</sub>O<sub>3</sub> content become high enough (12-18 wt%, depending on overall MO composition) to crystallize appreciable feldspar. During the process of exclusively mafic FC, the MO's mg ratio and [Mg+Fe] are dramatically lowered, but otherwise (especially if dry pressure is causing pyroxene to crystallize along with olivine) it does not evolve much. Hence, by the time the FAS formed as a series of MO flotation cumulates, the parent melt was uncommonly "ferroan" despite being "moderate" in all other respects (e.g., Ca/Na). The complete absence of sizeable geochemically ferroan rocks with complementary (low) modal feldspar among samples from the megaimpact-gardened lunar highlands is a key line of evidence in support of a lunar MO initially at least 100 km deep.

This model implies that the Mg-suite rocks formed by a comparatively normal variety of basaltic FC, probably in numerous, localized intrusions shortly after the era of MO crystallization and FAS genesis. Regardless of the degree of melting involved in the genesis of the primary melts, the prolonged, exclusively mafic FC involved in FAS genesis was seldom replicated, because these later magmas were prone to undergo assimilation reactions with the anorthositic FAS matter into which they intruded. Assimilation of FAS matter brought the Mg-suite intrusions to feldspar saturation early in the FC process, before the melt mg ratio could be driven down to the "ferroan" range [4]. Later FC proceeded along normal lines. The paradoxically high mg ratios of KREEPy rocks are consistent with the messy, mixing-assimilative aspects of this model, and confirm the volumetric importance of Mg-suite magmatism.

This model has not yet been challenged in any specific way, although obviously doubts remain. However, the doubts today come from those petrologists who question whether any of the ancient lunar cumulates formed from a MO. No one of late has argued that the MO model can still be applied to the Mg-suite as well as the FAS. Advocates of a MO-less early Moon [e.g., 5] seem to assume that the geochemical diversity is significant, but perhaps not truly bimodal. The MO-less scenario is often

described as "serial" magmatism, after Walker [6]. This term has fostered some confusion, because one can assume that a MO engendered the FAS, and still believe, as we do, that piecemeal, "serial" magmatism was responsible for the genesis of the Mg-suite [7].

Mixing-deconvolution for average highlands regolith implies at least 50%, and most likely about 70% of the crust is presently FAS (or FAS components in breccias). Korotev and Haskin [8] argued that the proportion of FAS must be <40%, but this conclusion was based on exceedingly dubious assumptions. The present Mg-suite may consist partly of assimilated FAS [4], so the original FAS volume was most likely 75% of the final crust volume. This still leaves 25% of the crust, or 2.5% of the Moon, to form out of "serial" melts from the deep interior. Unless the average degree of melting was extraordinarily high as the primary Mg-suite magmas formed, the combined source region must comprise a significant fraction of the Moon. Warren [1] inferred, based on averaged modes, plus the scarcity of lunar-crustal dunite (some of which would have to form, despite FAS assimilation, from initially ultramafic parent melts), that the average Al<sub>2</sub>O<sub>3</sub> content of Mg-suite plutons is at least nearly 18 wt%. Much of this might have been acquired by assimilation of roughly 30% FAS material (with ~30 wt% Al<sub>2</sub>O<sub>3</sub>), but the primary magmas are still required to have ~12-13 wt%. The requirement to produce this much post-MO, moderate-Al<sub>2</sub>O<sub>3</sub> melt out of the Moon's deep interior poses a problem for models that would have the entire Moon, or nearly the entire Moon, become molten, or even partly molten, as the Moon formed.

Even if the source region had retained a full bulk-silicate-Moon complement of  $Al_2O_3$ ,  $Al_{RSM} \sim 3$ wt%, the degree of melting to produce the average Mg-suite primary magma must be 3/12 = 25%. If 2.5%of the Moon is crust of Mg-intrusive origin, mass balance then implies that the total Mg-suite source region volume,  $V_{SR}$ , must have been at least 2.5/0.25 = 10% of the Moon. If instead the source regions were strictly high-mg cumulates from the early MO, the Al<sub>2</sub>O<sub>3</sub> contents of these source regions must have been approximately  $Al_{RSM}$  times the proportion of trapped liquid in the cumulates: thus, at most  $0.2 Al_{RSM}$ and more plausibly <0.1  $Al_{RSM}$  (i.e., 0.6 and more plausibly <0.3 wt%  $Al_2O_3$ ). In order for a source with 0.6 wt% Al<sub>2</sub>O<sub>3</sub> to generate primary magma with >12 wt% Al<sub>2</sub>O<sub>3</sub>, the degree of melting must be 5% or less. Mass balance then implies that  $V_{SR}$  must have been roughly 2.5/0.05 = 50% of the Moon. This cumulate-remelting scenario seems unlikely for numerous reasons. Available heat sources (impacts, delayed convective overturn of inverted density stratification of MO cumulates, possibly <sup>26</sup>Al) would not likely heat such a large volume to such a uniformly low degree of melting. Such a low-degree partial melt would not quickly or cleanly separate from the residual crystalline matrix. If such a large fraction of the mantle were involved in Mg-suite genesis, it is hard to explain why the Mg-suite magmas and mare basalts were so grossly dissimilar. The Mg-suite source region may well have overlapped the original base of magmasphere (= the MO plus an associated partially molten "magmifer" or "paracumulate" zone below). If so, the average source region  $Al_2O_3$  content was probably much less than  $Al_{BSM}$  but much greater than the average for the early high-mg cumulates from the MO. Thus,  $V_{SR}$  was most likely intermediate between the two estimates above: 30±15 vol% is our preferred, "best guess" value. Under this scenario, the magmasphere never extended deeper than ~600±200 km.

The Al<sub>2</sub>O<sub>3</sub> mass balance problem is almost equally severe if instead of early high-mg MO cumulates, the Mg-suite source regions are assumed to be residual solids from deep partial melting associated with the formation of the MO. Any deep zone subjected to a prior episode of differentiation, whether FC or partial melting, in the low-P interior of a Moon-sized body (little or no high-P stabilization of Al-rich phases such as majorite) is unlikely to retain much of its original Al<sub>2</sub>O<sub>3</sub>. Our conclusion that at least the Mg-suite portion of the lunar crust formed by post-MO "serial" magmatism implies that a major fraction of the deep interior of the Moon escaped even moderate-degree partial melting until shortly after the MO era. The Moon formed hot, but it was never even close to fully molten.

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GIANT AND LARGE IMPACTS IN THE CONTEXT OF PLANETARY FORMATION THEORY; G.W. Wetherill, DTM, Carnegie Institution of Washington, Washington, D.C.

A proper understanding of the magmatic and early differentiation history of the Earth, moon, and terrestrial planets will require synthesis of the knowledge acquired from geological and astronomical observations with quantitative theoretical models of star and planet formation. Progress toward such a goal has been achieved during recent years as a result of major contributions by a number of workers. A moderately obsolescent review of this work is available (1).

Of particular relevance to the subject of this workshop is the expected size and velocity distribution of the interplanetary projectiles during the late stages of planet formation. This will in turn be determined by the evolution of these distributions throughout the planet forming process. Even at this early stage of understanding, it seems clear that assumption of simple power-law mass distributions are certain to lead to incorrect conclusions. Furthermore, the lunar cratering evidence, valuable as it is for relatively late (i.e. < 4.2 b.y.) events, cannot provide information regarding stochastic events of potentially moon-destroying energy expected to be experienced by the early Earth.

It seems very likely that the early stages of terrestrial planet formation was marked by the rapid ( $\leq 10^5$  years) growth of an assemblage of "planetary embryos" of lunar to Mercury size. Altogether the mass distribution at that time appears to have been trimodal: these massive embryos, residual partly grown planetesimals of 10 to 100 km diameter, and a population of collision fragments of these planetesimals, extending down to the size of dust. The relative proportions of these populations is at present uncertain, but this question is being currently addressed. This brief early stage was characterized by the low impact velocities associated with a pre-planetary disk of bodies in nearly circular and coplanar orbits.

The onset of the late stage of planet formation was initiated by the embryos becoming sufficiently massive to perturb one another into crossing orbits, resulting in acceleration of the entire assemblage of bodies to velocities in the 1 to 10 km/sec range. On a ~ 108 year time scale this assemblage accumulated to form the present planets. During this process, the number of embryos was gradually reduced as they grew more massive, partly as a consequence of mutual collisions between embryos. Widespread, but not complete, mixing of material is predicted, including admixture of material from the present asteroidal region. A fourth population of bodies will be produced during this stage by the collisional fragmentation of smaller Mercury-size embryos. The growth, thermal, and impact history of the terrestrial planets

will be governed by the collisional and dynamical evolution of all four of these populations.

It is not likely that the growth of the Earth was characterized by gradual accumulation of small bodies, punctuated by a single moon-forming giant impact. Rather it would be expected that numerous major collisions between embryos would occur, and that some relatively small (e.g. lunar size) impacts may have been more energetic than the larger Mars-size impacts. In any case, it seems hard to escape widespread melting of the primordial Earth, but in detail the sequences of melting, mixing, crystallization, outgassing, and atmospheric-loss events are likely to have been complex.

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